



# Toxicant default guideline values for aquatic ecosystem protection

## Aluminium in marine water

Technical brief

October 2024

DRAFT

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### Contact

Australian Government Department of Climate Change, Energy, the Environment and Water  
GPO Box 3090 Canberra ACT 2601  
General enquiries: 1800 920 528  
Email [waterquality@dcceew.gov.au](mailto:waterquality@dcceew.gov.au)

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**New Zealand Government**



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## Summary

Aluminium (Al) is the most abundant metal in the Earth's crust and is widely distributed as aluminosilicates. It has little or no biological function. Aluminium enters the aquatic environment primarily through natural processes, such as weathering of rocks and volcanic activity. Aluminium also comes from anthropogenic sources, including mining, industrial processes using aluminium, and wastewater and drinking water treated with alum.

The previous Australian and New Zealand default guideline value (DGV) for aluminium in marine water was a low-reliability environmental concern level (ECL) of 0.5 µg/L. This was based on applying a safety factor of 200 to the lowest value of a limited dataset of mostly acute toxicity data for 6 species from 3 taxonomic groups (ANZECC and ARMCANZ 2000). There are now more data available on aluminium chronic toxicity to marine species, including a substantial number of Australasian species. This has enabled the derivation of improved DGVs compared to those in ANZECC and ARMCANZ (2000). The DGVs reported here build upon aluminium marine guideline values derived by Golding et al. (2015) and later updated by van Dam et al. (2018a).

Open-ocean concentrations of dissolved aluminium are typically in the range of nanograms per litre, while concentrations of 1–5 µg/L have been reported in uncontaminated coastal waters in Australia (Golding et al. 2015). In marine waters, aluminium speciation is dominated by soluble mononuclear hydroxy species ( $\text{Al}(\text{OH})_3$  and  $\text{Al}(\text{OH})_4^-$ ), with no polynuclear species detected. Concentrations of colloidal species in marine waters are typically extremely low (Golding et al. 2015), in contrast to freshwaters.

The chronic toxicity values of aluminium to marine species range across 3 orders of magnitude, from 14 µg/L for the sensitive diatom *Ceratoneis closterium* (72-hour IC<sub>10</sub> for growth; see Glossary and acronyms for definitions) (Harford et al. 2011) to 28,000 µg/L for the tolerant echinoderm *Heliocidaris tuberculata* (72-hour NOEC for larval development) (Golding et al. 2015). The solubility limit for aluminium in marine waters is around 500 µg/L (Angel et al. 2016), and both dissolved and some precipitated forms of aluminium are bioavailable and toxic to some species. For this reason, guideline values based solely on dissolved fractions of aluminium are not appropriately protective of aluminium toxicity. Thus, the DGVs reported here are based on both dissolved and precipitated forms of aluminium contributing to toxicity.

Very high reliability DGVs for total aluminium in marine waters were derived based on chronic EC<sub>10</sub>, IC<sub>10</sub> and NOEC data for 18 marine species belonging to 8 taxonomic groups, with a good fit of the species sensitivity distribution (SSD) to the toxicity data. The DGVs for 99%, 95%, 90% and 80% species protection are 9 µg/L, 37 µg/L, 72 µg/L and 160 µg/L, respectively. The 95% species-protection level for aluminium of 37 µg/L should be used when assessing ecosystems that are slightly to moderately disturbed.

# 1 Introduction

Aluminium is the most abundant metal in the Earth's crust and is widely distributed as aluminosilicates. It has little or no biological function (Gensemer and Playle 1999). Aluminium enters the aquatic environment primarily through natural processes, such as weathering of rocks and volcanic activity. Aluminium also comes from anthropogenic sources, including mining of bauxite and other ores, aluminium production (smelting and refining), fossil fuel combustion, industrial processes using aluminium, and wastewater and drinking water treated with alum (US EPA 2018). Aluminium is produced from alumina, which is refined from bauxite, the primary aluminium ore. As of 2022, Australia was the world's largest producer of bauxite (> 100 million tonnes per year), the second-largest producer of alumina (~20 million tonnes per year) and sixth-largest producer of aluminium (~1.5 million tonnes per year) (Australian Aluminium Council Ltd 2022). Bauxite is not mined in New Zealand, although aluminium is produced at one smelter near Invercargill on the South Island.

The chemistry and toxicity of aluminium in freshwaters have been widely studied, with reviews by Sposito 2020, Driscoll and Schecher 1990, Driscoll and Postek 1996 and Lazerte et al 1997. With increasing pH up to pH 6, aluminium speciation in freshwaters changes from mononuclear  $\text{Al}^{3+}$  and  $\text{Al}(\text{OH})^{2+}$  to  $\text{Al}(\text{OH})_2^+$  (Lazerte et al. 1997). Above pH 6, polynuclear aluminium species begin to form, with  $\text{Al}(\text{OH})_3$  forming at pH 7. Above pH 7, anionic  $\text{Al}(\text{OH})_4^-$  becomes increasingly dominant (Gensemer and Playle 1999; Wilson 2012).

Studies of aluminium speciation in marine waters are limited. In contrast to freshwaters, the speciation of aluminium in seawater is dominated by soluble mononuclear hydroxy species such as  $\text{Al}(\text{OH})_3$  (Millero et al. 2009),  $\text{Al}(\text{OH})_4^-$  (Millero et al. 2009) and  $\text{MgAl}(\text{OH})_4^+$  (Markich 2021). No polynuclear species have been detected. Colloidal species, if present, are at extremely low concentrations (Golding et al. 2015).

Open-ocean concentrations of dissolved aluminium are typically in the range of nanograms per litre and include measured concentrations of ~0.01–0.02  $\mu\text{g/L}$  at depths to 120 m in the Southern Ocean (Middag et al. 2011). Concentrations in uncontaminated coastal waters are generally higher, with concentrations of 1–5  $\mu\text{g/L}$  reported in Australia (Golding et al. 2015).

An important observation from aluminium toxicity and speciation studies is the dynamic nature of the solution chemistry of aluminium in marine waters. Although the solubility limit of aluminium in seawater is near 500  $\mu\text{g/L}$  (Angel et al. 2016), transient dissolved aluminium concentrations above this solubility limit persist for several days before precipitation and establishment of equilibrium solubility conditions (Angel et al. 2016). This has important implications for toxicity studies, which are typically conducted over periods of 2–5 days, with pre-equilibration of test solutions being required to mimic field conditions. It also means that organisms are exposed to a mixture of dissolved and particulate aluminium species (Angel et al. 2016), both of which are toxic to some species (Golding et al. 2015).

Some particulate forms of aluminium exist in seawater as mineralised clay, soil and sediment in suspension. These are assumed to be less bioavailable and toxic than colloidal aluminium and other aluminium precipitates (Gensemer and Playle 1999). To prevent the inclusion of these forms of particulate aluminium in a comparison of aquatic aluminium concentrations with DGVs for

aluminium, a 0.45- $\mu\text{m}$  filtered seawater sample, which removes the mineralised aluminium component, should be compared with DGVs (see section 4.3). Although a study by Rodriguez et al. (2019) suggested that extraction at pH 4 best reflects the bioavailable fraction in freshwater samples, further research is needed before this could be applied to marine waters.

The previous Australian and New Zealand DGV for aluminium in marine water was a low reliability ECL of 0.5  $\mu\text{g/L}$ . This was based on applying a safety factor of 200 to a 96-hour LC50 of 97  $\mu\text{g/L}$  for the annelid *Ctenodrilus serratus* from a limited dataset of one chronic toxicity value and 11 acute toxicity values for 6 species from 3 taxonomic groups (ANZECC and ARMCANZ 2000). There are now more data available on the chronic toxicity of aluminium to marine species, including a substantial number of temperate and tropical Australasian species. This has enabled the derivation of improved DGVs compared to those in ANZECC and ARMCANZ (2000). The aluminium marine DGVs reported here supersede the ANZECC and ARMCANZ (2000) ECL, and they build upon guideline values derived by Golding et al. (2015) and later updated by van Dam et al. (2018a).

## 2 Aquatic toxicology

### 2.1 Mechanisms of toxicity

Aluminium is a non-essential metal that causes harmful effects to aquatic life at elevated concentrations. The US EPA (2018) reviewed known and suspected mechanisms of toxicity of aluminium. In invertebrates, aluminium disrupts salt balance, resulting in a loss of sodium and possibly other ions. Aluminium also reduces respiratory efficiency in invertebrates. For fish, the gill is the primary site of aluminium toxic action, affecting the ionoregulatory, osmoregulatory and respiratory systems (US EPA 2018). This occurs at both acidic and alkaline pH and so is relevant for both freshwater and marine species. Overall, however, the specific mechanisms of aluminium toxicity at alkaline pH are not well understood.

Both dissolved and some precipitated forms of aluminium are bioavailable and toxic to some species (e.g. Golding et al. 2015; Gillmore et al. 2016; US EPA 2018). For this reason, guideline values based solely on dissolved fractions of aluminium are not appropriately protective of aluminium toxicity.

### 2.2 Toxicity

As noted in section 1, there were limited data on the toxicity of aluminium to marine species prior to 2000. The majority of studies assessed acute rather than chronic toxicity, and none measured aluminium concentrations nor considered speciation of aluminium. Since 2000, there have been a number of publications on the toxicity of aluminium in marine waters. The most comprehensive of these were by Golding et al. (2015), who reported toxicity tests for 9 species from 6 taxonomic groups, and van Dam et al. (2018a), who summarised toxicity data for 17 species from 10 taxonomic groups.

The chronic toxicity values of aluminium to marine species range across 3 orders of magnitude, from 14 µg/L for a sensitive tropical strain of the diatom *C. closterium* (72-hour growth rate IC10) (Harford et al. 2011) to ≥ 28,000 µg/L for the tolerant echinoderm *Heliocidaris tuberculata* (72-hour larval development NOEC) (Golding et al. 2015). Other sensitive species include the echinoderm *Paracentrotus lividus*, with an EC10 of 32 µg/L (72-hour embryo abnormalities) (Caplat et al. 2010; data re-analysed for the current derivation), the oyster *Saccostrea commercialis* (now *Saccostrea glomerata*), with a NOEC of 100 µg/L (72-hour embryo development) (Wilson and Hyne 1997) and the snail *Nassarius dorsatus*, with an EC10 of 115 µg/L (96-hour growth rate) (Trenfield et al. 2016). Other tolerant species include the brown algae *Hormosira banksii* and *Ecklonia radiata*, with a NOEC and EC10 of ≥ 9,800 µg/L and 6,800 µg/L, respectively (72-hour germination success) (Golding et al. 2015). A coral species (*Acropora tenuis*) has also been assessed, with a reported EC10 of 1,300 µg/L (18-hour EC10) (Negri et al. 2011). Acute toxicity data for marine fish suggest they are also tolerant of aluminium, with no adverse effects on growth of the barramundi *Lates calcarifer* and the damselfish *Acanthochromis polyacanthus* over 7-day exposure to an aluminium concentration of < 10,000 µg/L (Golding et al. 2015). However, there are no studies of longer exposure duration for fish to provide an estimate of chronic toxicity.

The high sensitivity to aluminium of *C. closterium* has been checked and confirmed on several occasions. Golding et al. (2015) reported a 72-hour IC10 (growth rate) of 18 µg/L for a temperate strain, which was consistent with the sensitivity of a tropical strain (14 µg/L) tested by Harford et al. (2011). Subsequently, Gillmore et al. (2016) reported a 72-hour IC10 (growth rate) of 80 µg/L for the temperate strain and, although higher (less toxic) than that reported by Harford et al. (2011) and Golding et al. (2015), that value was still lower than for all but one other species reported in the literature. The difference in toxicity may have been due to the initial algal density, as Gillmore et al. (2016) also found that aluminium toxicity to *C. closterium* was higher at the higher initial density used by Harford et al. (2011) and Golding et al. (2015) ( $10^4$  cells/ml) compared to that used by Gillmore et al. (2016) ( $10^3$  cells/ml).

The high sensitivity of the urchin *P. lividus* (Caplat et al. 2010) contrasts with the very low sensitivity reported for another urchin species, *H. tuberculata* (Golding et al. 2015), with a difference of 3 orders of magnitude in toxicity estimates. Unfortunately, there are no other data for these species to verify these estimates.

van Dam et al. (2018a) compared the toxicity of aluminium to temperate and tropical species. Based on a direct comparison of toxicity estimates across the range of species for which data existed, tropical species were more sensitive to aluminium than temperate species (7 out of the 11 most sensitive data points were for tropical species). However, distinct differences between the 2 datasets confounded the comparison, and there was insufficient evidence to suggest that tropical species were generally more sensitive than temperate species (but also see section 3).

Subsequent to the completion of the current DGV derivation, Markich (2021) published 48-hour NECs based on larval development for 10 bivalve mollusc species comprising 4 clams, 2 oysters, 2 cockles, one mussel and one scallop. The NECs differed by less than a factor of 3, from 88 to 235 µg/L. This range of sensitivity was similar to that based on previously published data for the bivalves *S. glomerata* (72-hour larval development NOEC of 100 µg/L) (Wilson and Hyne 1997), *Mytilus edulis plannulatus* (72-hour larval development EC10 of 250 µg/L) (Golding et al. 2015) and *Saccostrea echinata* (72-hour larval development EC10 of 410 µg/L) (Golding et al. 2015). Thus, bivalves have a relatively narrow range of sensitivity and are consistently among the taxa most sensitive to aluminium.



### 3 Factors affecting toxicity

At a typical seawater pH of 8.1, model calculations by Millero et al. (2009) showed inorganic dissolved aluminium speciation to comprise aluminate,  $\text{Al}(\text{OH})_4^-$  (68%) and a soluble, neutral hydroxide species,  $\text{Al}(\text{OH})_3^0$  (32 %). It is noteworthy that cationic species that dominate aluminium speciation in acidic freshwaters are not important in seawater, where the higher pH means that neutral or anionic species dominate.

Field studies have provided further evidence that the main forms of dissolved aluminium in coastal systems are small species (probably  $\text{Al}(\text{OH})_4^-$  and soluble  $\text{Al}(\text{OH})_3^0$ ) (Angel et al. 2016). Markich (2021) has suggested that alkaline earth-aluminate species (e.g.  $\text{MgAl}(\text{OH})_4^+$ ) may amount to 30–40% of the dissolved aluminium. Unlike in freshwaters, the concentrations of colloidal aluminium species were very low, and this was supported by observations made in the laboratory.

Complexing agents, such as fluoride, citrate and humic substances, reduce the availability of aluminium to organisms, making it less toxic. Silica can also reduce the toxicity of aluminium to fish through the formation of stable hydroxyaluminosilicates (Gensemer and Playle 1999). Given the generally low concentrations of dissolved organic carbon (DOC) in coastal seawater, organic complexation may not be a significant modifier of speciation of aluminium. Moreover, there are few, if any, available data on the effect of DOC on the toxicity of aluminium to marine species. Nevertheless, where higher concentrations of complexing agents are present in marine water, their influence on aluminium toxicity may need to be considered on a site-specific basis (van Dam et al. 2018a).

The solubility of aluminium is slightly higher at higher temperatures (Santore et al. 2018). Therefore, van Dam et al. (2018a) hypothesised that aluminium bioavailability and toxicity might be higher in tropical climates than temperate climates. However, as noted in section 2.2, there is insufficient evidence at present to confirm this. Trenfield et al. (2015, 2016) found that temperature can influence aluminium toxicity, although the effect was different to that hypothesised by van Dam et al. (2018a). Increasing the temperature from 24 to 31 °C resulted in only a minor reduction in toxicity to the microalga *Tisochrysis lutea* (formerly *Isochrysis galbana*), but there was a greater reduction in toxicity to larvae of the snail *N. dorsatus*. However, this may have been due to the increased stress of the lower temperature to these 2 tropical species, rather than an interaction between temperature and aluminium toxicity. At present, there is insufficient evidence to justify the derivation of different DGVs for aluminium based on temperature or climatic regions.

The toxicity of aluminium to marine (and freshwater) species can be caused by both dissolved and particulate (precipitated and colloidal) aluminium (Angel et al. 2016; Golding et al. 2015; US EPA 2018; van Dam et al. 2018a). With only a limited number of species having a concentration–response curve below the solubility limit, it was not possible to derive DGVs for dissolved aluminium alone. By using all the toxicity data based on measured total aluminium in the toxicity tests, DGVs were derived that protect species from dissolved and particulate (precipitated and colloidal) aluminium.

## 4 Default guideline value derivation

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

### 4.1 Toxicity data used in derivation

A comprehensive literature search obtained data on the chronic toxicity of aluminium to marine organisms. Marine toxicity data for 18 species (8 taxonomic groups) from 10 studies passed the quality-assessment and screening processes. Chronic toxicity data were available for 12 temperate and 7 tropical organisms, which included temperate and tropical strains of the diatom *C. closterium* (Table 1, Appendix A). A comparison of the temperate and tropical datasets (van Dam et al. 2018a) led to the conclusion that the DGVs should be derived from the combined temperate and tropical dataset.

Acute toxicity data, including data for the fish *L. calcarifer* and *A. polyacanthus* (Golding et al. 2015), were not used for the derivation because there were sufficient chronic toxicity data for other species and taxonomic groups to meet the minimum data requirements (Warne et al. 2018).

For the brown alga *H. banksii* and the sea urchin *H. tuberculata*, no effects were observed up to and including the highest tested concentration. Therefore, the highest test concentration was used as the NOEC for both species.

The 4-day exposure duration for the growth test of the snail *N. dorsatus* reported by Trenfield et al. (2016) would typically be considered an acute exposure duration. However, Warne et al. (2018) recognised that the typical acute/chronic test classification predominantly applies to temperate species. Tropical species may experience much faster early development, so chronic toxicity tests using tropical organisms may be of shorter duration than those for temperate species. Thus, as *N. dorsatus* is a tropical species, the 4-day growth response was accepted as an estimate of chronic toxicity, and it was included in the dataset used for the DGVs derivation.

For several of the tropical species (e.g. *N. dorsatus* and the microalga *T. lutea*), there were aluminium toxicity data for 2 or 3 temperatures. Rather than always using the lowest value or the geometric mean of the values from across the different temperatures, the value generated from the temperature that most closely represented the natural environmental temperature for the species was used. Given that the tested species were tropical strains and, in the case of the snail, the test organisms appeared stressed at the lower temperature, only the 28 °C data for both species were included in the dataset for the derivation of the DGVs.

An EC10 for the sea urchin *P. lividus* was estimated from a re-analysis of the concentration–response data for developmental defects presented by Caplat et al. (2010), because the paper did not report any toxicity estimates. The re-analysis is presented in Appendix B and resulted in an EC10 of 32 µg/L.

The data from all studies except one were based on measured total aluminium concentrations, because of the reasons discussed earlier that guideline values based solely on dissolved fractions of aluminium are not appropriately protective of aluminium toxicity. Wilson and Hyne (1997) reported toxicity estimates for *S. glomerata* based on nominal concentrations but noted that the nominal

values deviated by less than 10% of measured values. Consequently, the data were acceptable for inclusion in the derivation of the DGVs.

The aluminium toxicity data for 10 bivalves recently published by Markich (2021) were not used in the derivation, for the following reasons. The Markich (2021) NECs for bivalves (88–235 µg/L) are tightly congregated within the 10th to 20th percentile of the DGV dataset, which represents a similar portion of the dataset occupied by the bivalve data already included in the dataset (*S. glomerata* – NOEC of 100 µg/L, *M. edulis plannulatus* – EC10 of 250 µg/L and *S. echinata* – EC10 of 410 µg/L). Thus, the existing bivalve data adequately represents the sensitivity of bivalves to aluminium. To include the additional bivalve species from Markich (2021) would result in 12 of the 26 final toxicity values being for bivalves, which would be an unacceptable over-representation of bivalves. Additionally, all of the bivalve species reported by Markich (2021) are protected by the derived 99% and 95% species-protection DGVs.

The available evidence on aluminium toxicity and mechanisms of toxicity to marine species (section 2) indicated that the distribution of toxicity is unimodal, and so the full dataset could be used to derive the DGVs.

The final dataset comprised chronic toxicity data for 18 species from 8 taxonomic groups, comprising 3 diatoms, 3 microalgae, 2 brown algae, 3 bivalve molluscs, one gastropod mollusc, 2 crustaceans, 2 cnidarians and 2 echinoderms. Except for *P. lividus*, all species represented in the dataset occur in Australian temperate or tropical marine waters. The toxicity data included 15 chronic EC/IC10 values and 3 chronic NOEC values. Although Warne et al. (2018) recommended to exclude NOECs where > 8 EC/IC10 data are available (for ≥ 5 species from ≥ 4 taxonomic groups), the 3 NOEC values were included so that data for an additional 3 species (*H. banksii*, *H. tuberculata* and *S. glomerata*) could be incorporated. One of these, *S. glomerata*, was the third-most sensitive species in the dataset. Table 1 provides a summary of the toxicity data used to derive the DGVs. Further details on the data that passed the quality-assessment and screening process and were used to derive the DGVs are presented in Appendix A. Details of the data-quality assessment and the data that passed the quality assessment are provided as supporting information.

**Table 1 Summary of chronic toxicity data values used to derive the guideline values for aluminium**

Taxonomic group	Species	Life stage	Duration (h)	Toxicity measure <sup>a</sup> (endpoint)	Final toxicity value (µg/L)
<b>Temperate organisms</b>					
Diatom	<i>Ceratoneis closterium</i>	Exponential phase	72	IC10 (growth rate)	27 <sup>b</sup>
	<i>Minutocellus polymorphus</i>	Exponential phase	72	IC10 (growth rate)	610 <sup>b</sup>
	<i>Phaeodactylum tricornutum</i>	Exponential phase	72	IC10 (growth rate)	2,100
Microalga	<i>Tetraselmis</i> sp. (green flagellate)	Exponential phase	72	IC10 (growth rate)	3,200
	<i>Dunaliella tertiolecta</i>	Exponential phase	72	IC10 (growth rate)	1,400
Brown alga	<i>Hormosira banksii</i> (Neptune's necklace)	Embryo	72	NOEC (germination)	9,800
	<i>Ecklonia radiata</i> (kelp)	Embryo	72	IC10 (germination)	6,800
Echinoderm (sea urchin)	<i>Heliocidaris tuberculata</i>	Embryo	72	NOEC (embryo development)	28,000
	<i>Paracentrotus lividus</i>	Embryo	72	NOEC (embryo abnormality)	32
Mollusc (bivalve)	<i>Mytilus edulis plannulatus</i> (common mussel)	Embryo	72	EC10 (embryo development)	250
	<i>Saccostrea echinata</i> (blacklip oyster)	Embryo	72	EC10 (embryo development)	410
	<i>Saccostrea glomerata</i> (Sydney rock oyster) <sup>c</sup>	Embryo	72	NOEC (embryo development)	100
<b>Tropical organisms</b>					
Diatom	<i>Ceratoneis closterium</i>	Exponential phase	72	IC10 (growth rate)	27 <sup>b</sup>
Microalga	<i>Tisochrysis lutea</i> <sup>d</sup>	Exponential phase	72	IC10 (growth rate)	640
Cnidarian (coral)	<i>Acropora tenuis</i> (branched coral)	Larva	18	EC10 (metamorphosis)	1,300
Cnidarian (anemone)	<i>Exaiptasia diaphana</i> (glass anemone) <sup>e</sup>	Larva	336	EC10 (reproduction)	817
Mollusc (gastropod)	<i>Nassarius dorsatus</i>	Embryo-larval	96	EC10 (growth rate)	115
Crustacean (barnacle)	<i>Amphibalanus amphitrite</i>	Nauplii	96	EC10 (larval development)	416
Crustacean (crab)	<i>Coenobita variabilis</i> (Australian land hermit crab)	Zoea (larva)	72	EC10 (larval development)	312

<sup>a</sup> The measure of toxicity being estimated/determined. EC10: 10% effect concentration; IC10: 10% inhibition concentration; NOEC: no-observed-effect concentration.

<sup>b</sup> Value represents a geometric mean. See Appendix A for details.

<sup>c</sup> Formerly *Saccostrea commercialis*.

<sup>d</sup> Formerly *Isochrysis galbana*.

<sup>e</sup> Formerly *Exaiptasia pallida*.

## 4.2 Species sensitivity distribution

Figure 1 shows the cumulative frequency (species sensitivity) distribution (SSD) of the 18 marine chronic toxicity values for aluminium reported in Table 1. The SSD was plotted using the Burrlioz 2.0 software. The model was judged to provide a good fit to the data (Figure 1).

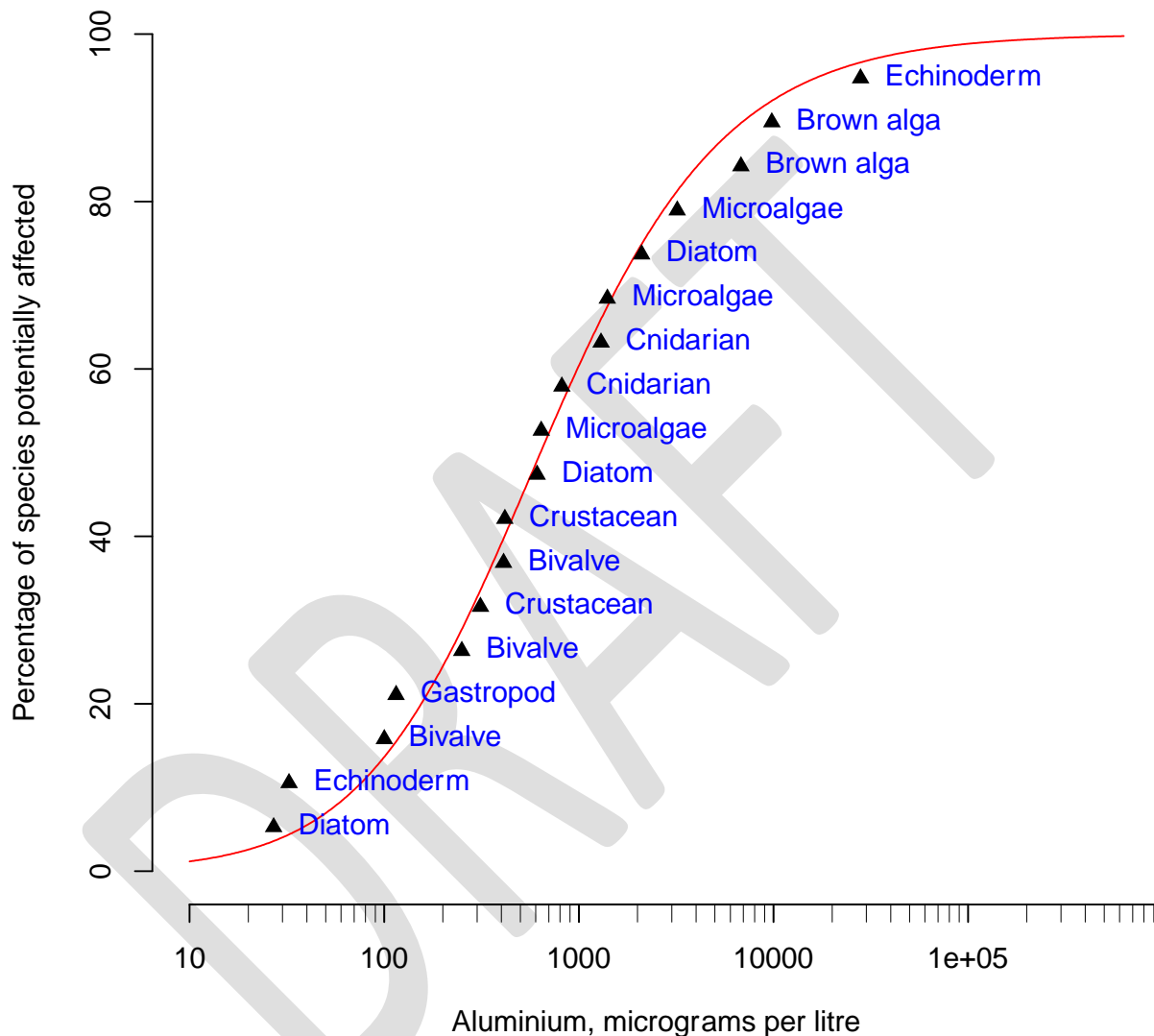


Figure 1 Species sensitivity distribution (from Burrlioz 2.0) for chronic toxicity data for aluminium in marine water

## 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](#) (ANZG 2018).

Table 2 shows the DGVs for 99%, 95%, 90% and 80% species-protection values for aluminium in marine waters. The DGVs relate to total aluminium and protect species from both dissolved and precipitated forms of aluminium. The DGVs are well below the solubility limit of aluminium in seawater, and so the total concentration will comprise mostly dissolved aluminium up to an environmental concentration at least 500 µg/L. Therefore, a dissolved aluminium measurement (operationally defined as 0.45-µm-filtered measurement) of an environmental sample should be appropriate for comparison with the DGVs. This will ensure that non-bioavailable, mineralised forms of aluminium are not included in the sample measurement. However, total and possibly pH-2 extraction analyses (see Appendix C) would also be required if the objective was to characterise aluminium speciation in the seawater sample rather than to just compare the result with a DGV.

The 95% species-protection value is twice as high as the toxicity value for the most sensitive species, *C. closterium*. However, the available evidence suggests that this species is indeed extremely sensitive relative to most other species and is likely to truly lie below the lower 5th percentile of sensitivity. As such, the 95% species-protection DGV of 37 µg/L should be used when assessing ecosystems that are slightly to moderately disturbed.

There is insufficient evidence of climatic differences in aluminium toxicity, so the DGVs are applicable to both temperate and tropical marine waters.

**Table 2 Toxicant default guideline values for aluminium in marine water with very high reliability**

Level of species protection (%)	DGV for aluminium in marine water (µg/L) <sup>a</sup>
99	9
95	37
90	72
80	160

<sup>a</sup> The DGVs were derived using the BurrIioz 2.0 software and rounded to 2 significant figures.

#### 4.4 Reliability classification

The DGVs for aluminium in marine water have a very high reliability classification (Warne et al. 2018) based on the outcomes for the following 3 criteria:

- sample size – 18 (preferred)
- type of toxicity data – chronic EC10, IC10, NOEC
- SSD model fit – good (Burr Type III).

## Glossary and acronyms

Term	Definition
Acute toxicity	A lethal or adverse sub-lethal effect that occurs as the result of a short (relative to the organism's life span) exposure to a chemical. Refer to Warne et al. (2018) for examples of acute exposures.
Acute-to-chronic ratio	The species' mean acute value (LC50/EC50) divided by the chronic value (NOEC) for the same species.
Chronic toxicity	A lethal or sub-lethal adverse effect that occurs as the result of exposure to a chemical for a period of time that is a substantial portion of the organism's life span or an adverse sub-lethal effect on a sensitive early life stage. Refer to Warne et al. (2018) for examples of chronic exposures.
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 value), in the <i>Australian and New Zealand Guidelines for Fresh and Marine Water Quality</i> . Formerly known as 'trigger values'.
DOC	Dissolved organic carbon.
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.
ELC	Environmental concern level.
Endpoint	The specific response of an organism that is measured in a toxicity test (e.g. mortality, growth, reproduction, a particular biomarker).
Guideline value (GV)	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.
Humic substances	Organic substances only partially broken down that occur in water mainly in a colloidal state. Humic acids are large-molecule organic acids that dissolve in water.
ICx	The concentration of a substance in water or sediment that is estimated to produce an x% inhibition of the response being measured in test organisms relative to the control response, under specified conditions.
LCx	The concentration of a substance in water or sediment that is estimated to be lethal to x% of a group of test organisms relative to the control response, under specified conditions.
LOEC (lowest-observed-effect concentration)	The lowest concentration of a chemical used in a toxicity test that has a statistically significant ( $p \leq 0.05$ ) adverse effect on the exposed population of test organisms as compared with the controls. All higher concentrations should also cause statistically significant effects.
NEC (no-effect concentration)	The maximum concentration of a toxicant that causes no adverse effect in a target organism.
NOEC (no-observed-effect concentration)	The highest concentration of a toxicant used in a toxicity test that does not have a statistically significant ( $p > 0.05$ ) effect on the exposed population of test animals as compared to the controls. The statistical significance is measured at the 95% confidence level.
Site-specific	Relating to something that is confined to, or valid for, a particular place. Site-specific trigger values are relevant to the location or conditions that are the focus of a given assessment.

<b>Term</b>	<b>Definition</b>
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.

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## Appendix A: toxicity data that passed the screening and quality assessment

**Table C1 Summary of toxicity data that passed the screening and quality assurance processes and were used to derive the default guideline values for aluminium in marine water**

Taxonomic group (phylum or clade)	Species	Life stage	Exposure duration (hours)	Test medium <sup>a</sup>	Test endpoint	Toxicity estimate	pH	Temperature (°C)	Toxicity value (µg/L total Al)	Reference
Gyrista (diatom)	<i>Ceratoneis closterium</i> – temperate strain	Exponential phase, 10 <sup>4</sup> cells/mL	72	Seawater	Growth rate inhibition	IC10	8.2	21	18	Golding et al. (2015)
	<i>Ceratoneis closterium</i> – temperate strain	Exponential phase, 10 <sup>3</sup> cells/mL	72	Seawater	Growth rate inhibition	IC10	8.2	21	80	Gillmore et al. (2016)
	<i>Ceratoneis closterium</i> – tropical strain	Exponential phase, 10 <sup>4</sup> cells/mL	72	Seawater	Growth rate inhibition	IC10	8.2	32	14	Harford et al. (2011)
									<b>27</b>	<b>Geometric mean; value used in SSD</b>
Gyrista (diatom)	<i>Minutocellus polymorphus</i>	Exponential phase, 10 <sup>4</sup> cells/mL	72	Seawater	Growth rate inhibition	IC10	8.2	21	690	Golding et al. (2015)
		Exponential phase, 10 <sup>3</sup> cells/mL	72	Seawater	Growth rate inhibition	IC10	8.2	21	540	Gillmore et al. (2016)
									<b>610</b>	<b>Geometric mean; value used in SSD</b>
Gyrista (diatom)	<i>Phaeodactylum tricornutum</i>	Exponential phase, 10 <sup>3</sup> cells/mL	72	Seawater	Growth rate inhibition	IC10	8.2	21	2,100	Gillmore et al. (2016)
Chlorophyta (microalga)	<i>Tetraselmis</i> sp.	Exponential phase, 10 <sup>4</sup> cells/mL	72	Seawater	Growth rate inhibition	IC10	8.2	21	3,200	Golding et al. (2015)

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

Taxonomic group (phylum or clade)	Species	Life stage	Exposure duration (hours)	Test medium <sup>a</sup>	Test endpoint	Toxicity estimate	pH	Temperature (°C)	Toxicity value (µg/L total Al)	Reference
Chlorophyta (microalga)	<i>Dunaliella tertiolecta</i>	Exponential phase, 10 <sup>4</sup> cells/mL	72	Seawater	Growth rate inhibition	IC10	8.2	21	1,400	Golding et al. (2015)
Chlorophyta (microalga)	<i>Tisochrysis lutea</i> <sup>e</sup>	Exponential phase, 3 × 10 <sup>3</sup> cells/mL	72	Seawater	Growth rate inhibition	IC10	8.2	28	640 <sup>a</sup>	Trenfield et al. (2015)
Gyrista (brown alga)	<i>Hormosira banksii</i>	Embryo	72	Seawater	Germination success	Chronic NOEC	8.2	18	9,800	Golding et al. (2015)
Gyrista (brown alga)	<i>Ecklonia radiata</i>	Embryo	72	Seawater	Germination success	IC10	8.2	18	6,800	Golding et al. (2015)
Cnidaria	<i>Acropora tenuis</i>	Larva	18	Seawater	Metamorphosis	EC10	8.2	32	1,300	Negri et al. (2011)
Cnidaria	<i>Exaiptasia diaphana</i> <sup>d</sup>	Larva	336	Seawater	Reproduction	EC19	8.1	28	817	Trenfield et al. (2017)
Echinodermata	<i>Heliocidaris tuberculata</i>	Embryo	72	Seawater	Development	Chronic NOEC	8.2	20	28,000	Golding et al. (2015)
Echinodermata	<i>Paracentrotus lividus</i> <sup>c</sup>	Embryo	72	Seawater	Developmental defects	EC10	8.2	18	32 <sup>c</sup>	Caplat et al. (2010)
Mollusca (bivalve)	<i>Mytilus edulis plannulatus</i>	Embryo	72	Seawater	Development	EC10	8.2	20	250	Golding et al. (2015)
Mollusca (bivalve)	<i>Saccostrea echinata</i>	Embryo	72	Seawater	Development	EC10	8.2	20	410	Golding et al. (2015)
Mollusca (bivalve)	<i>Saccostrea glomerata</i> <sup>b</sup>	Embryo	48	Seawater	Development	Chronic NOEC	8.2	24	100	Wilson and Hyne (1997)
Mollusca (gastropod)	<i>Nassarius dorsatus</i>	Larva	96	Seawater	Growth rate	EC10	8.2	27	115 <sup>a</sup>	Trenfield et al. (2016)
Arthropoda (crustacean)	<i>Amphibalanus amphitrite</i>	Nauplii (larva)	96	Seawater	Transition to cyprid	EC10	8.2	29	416	van Dam et al. (2016)
Arthropoda (crustacean)	<i>Coenobita variabilis</i>	Zoea (larva)	144	Seawater	Development	EC10	8.1	28	312	van Dam et al. (2018b)

<sup>a</sup> The EC10 at 27 °C /28 °C was selected over the EC10s at other temperatures, because the other temperatures were deemed to be outside the species' optimal thermal tolerance range and caused or may have caused additional stress to the test organisms.

<sup>b</sup> Formerly *Saccostrea commercialis*.

<sup>c</sup> Reported value based on a re-analysis of the published toxicity data. See Appendix B for details.

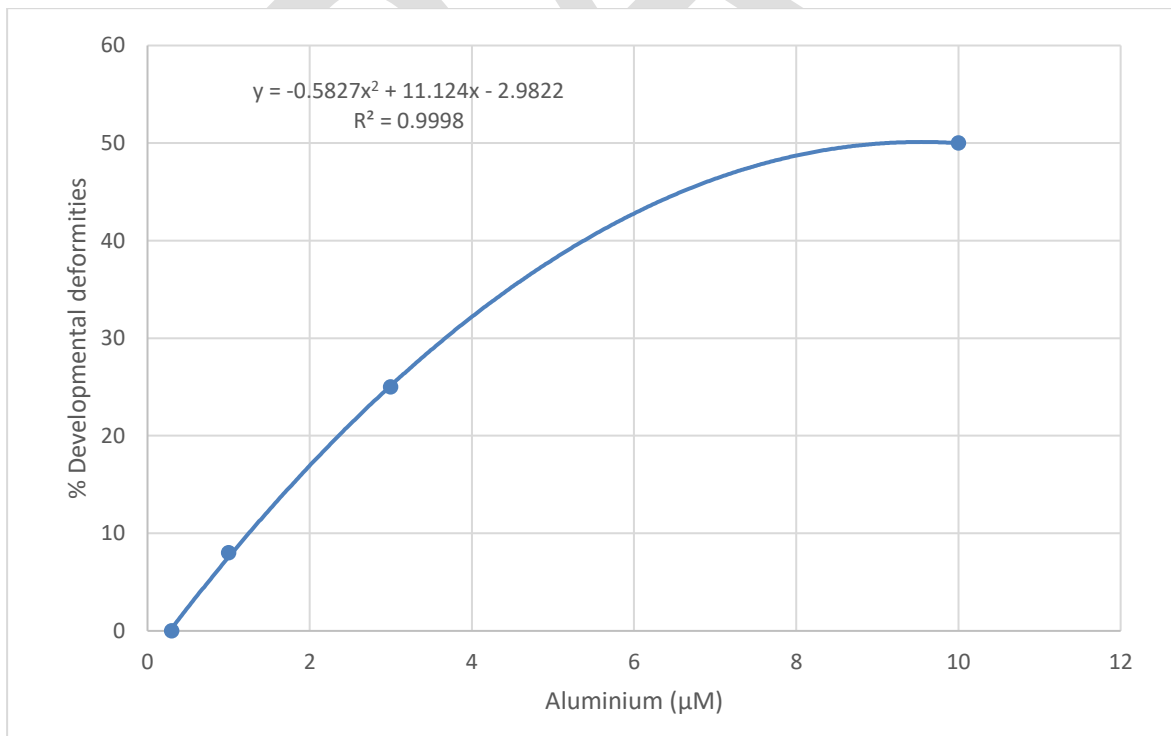
<sup>d</sup> Formerly *Exaiptasia pallida*.

<sup>e</sup> Formerly *Isochrysis galbana*.

## Appendix B: re-analysis of toxicity data for *Paracentrotus lividus*

Caplat et al. (2010) assessed the toxicity of aluminium to the purple sea urchin *P. lividus*. Although several endpoints were assessed, the analysis presented here is based on the developmental-defects endpoint following 72-hour exposure to aluminium sulfate. Developmental defects included malformed larvae, mostly affected in skeletal differentiation, and embryos and larvae unable to reach the pluteus stage (i.e. abnormal blastulae or gastrulae) and, therefore, the endpoint was ecologically relevant. The effect of a control and 4 (measured) aluminium concentrations (i.e. 0 µg/L, 8 µg/L, 27 µg/L, 81 µg/L and 270 µg/L; reported by Caplat et al. 2010 as 0 µM, 0.3 µM, 1 µM, 3 µM and 10 µM, respectively) on developmental defects was assessed over a 72-hour exposure period. Full details are provided by Caplat et al. (2010).

The percent developmental defects for each concentration was estimated from Figure 2 of Caplat et al. (2010). The estimated values represented the average of 12 replicates for each concentration. Without the individual replicate data, no estimate of error for the EC10 could be calculated. A 2-order polynomial regression (Excel v16.52) was used to model the concentration–response data normalised to the control response (Figure B1). The regression relationship had an  $r^2$  value of > 0.99, and the regression equation yielded an EC10 of 1.2 µM aluminium or approximately 32 µg/L. This value was used for *P. lividus* in the dataset that was used to derive the DGVs for aluminium in marine water.



**Figure B1 Aluminium toxicity data concentration–response curve for % developmental defects in *Paracentrotus lividus* larvae**

## Appendix C: water-quality assessment for sparingly soluble metals

A number of metals have low solubility in freshwater and marine water but have been found to be toxic at concentrations above their solubility limit. Therefore, the derivation of guideline values for those metals included data for which toxicity was at least in part due to particulate (precipitated) metals. Examples include iron(III) in marine water (solubility < 0.03 µg/L; Liu and Millero 2002), iron(III) in freshwater (solubility < 0.05 µg/L; Phippen et al. 2008), chromium(III) in freshwater (solubility < 5 µg/L; Rai et al. 1989) and aluminium in marine water (solubility ~500 µg/L; Angel et al. 2016).

For iron and chromium, the DGVs are above the solubility limits under oxic conditions and neutral pH. Measuring total metal concentrations to compare with these DGVs requires a method that discriminates between precipitated metals and metals in mineralised forms that are not likely to be bioavailable. This is normally a cold, dilute acid (pH-2) extraction (e.g. as per US EPA 1991) that will solubilise precipitated metal oxyhydroxides, including those that become adsorbed to other substrates such as mineralised forms or particulate (or colloidal) organic matter (Markich et al. 2002). A total-recoverable-metals analysis (concentrated acid digestion) should not be used, as this will overestimate the precipitated metals fraction by also including the digested mineralised forms, potentially leading to false exceedance of the DGV. At least in the case of iron and chromium, 0.45-µm sample filtration is not a recommended step, as it will exclude precipitated metal that might be contributing to toxicity, potentially leading to false compliance with the DGV.

A recent study by Balsamo Crespo et al. (2023) demonstrated that a 2-hour extraction of an unfiltered sample at pH 2 adequately discriminated non-mineralised iron in freshwaters. These results were subsequently confirmed in another study specifically commissioned to address public comments on the iron in freshwater DGVs relating to the appropriate chemical analysis method, although a 16-h extraction period was recommended (ANZG 2024). Another study by Rodriguez et al. (2019) reported that, for the analysis of aluminium in freshwater, a pH-4 extractable fraction best correlated with the toxic fraction. However, there is currently no accepted standard analytical method that employs a pH-4 extraction. Moreover, for iron, Balsamo Crespo et al. (2023) found that the pH 2 method performed better than the pH 4 method. In marine waters, buffering to pH 4 is possible but difficult (due to the carbonate buffer system having large pH changes around pH 4) and has yet to be fully investigated. Acidifying to pH 2 is less problematic. Consequently, until further validation studies on the most appropriate sample treatment are published, the pH-2 extraction method described in ANZG (2024) is adequate for sparingly soluble metals in both freshwaters and marine waters. There is a low risk of toxicity if the pH-2 extractable fraction does not exceed the DGV, but there is potential for toxicity if the DGV is exceeded.

Notably, for aluminium in marine water, the total bioavailable concentrations in contaminated water will generally be below the solubility limit of approximately 500 µg/L. Therefore, analysis of a 0.45-µm-filtered fraction should exclude the mineralised component (i.e. aged, not recently precipitated particulates) and will likely be appropriate for comparison with DGVs. However, if the objective is to

characterise aluminium speciation in marine water, then total and possibly the pH 2 extraction analyses would also be required.

The [Water Quality Management Framework](#) provides the opportunity for operators and proponents to [improve DGVs](#) or [develop site-specific guideline values](#) where the DGVs are not appropriate (e.g. where they do not reflect local conditions), in consultation with the regulator and other relevant stakeholders (ANZG 2018).

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