



Australian & New Zealand **GUIDELINES FOR** 

# **Toxicant default guideline values for aquatic ecosystem protection**

### Nickel in marine water

Technical brief July 2024

Water Quality Guidelines is a joint initiative of the Australian and New Zealand governments, in partnership with the Australian states and territories.

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## **Contents**



## Summary

Nickel is a commonly occurring natural element that is essential to some organisms. Nickel is mined and processed globally and used for many purposes, including the production of alloys, food preparation equipment, mobile telephones, batteries, medical equipment, transport, buildings and power generation. Anthropogenic sources of nickel include motor vehicle emissions, landfills, sewage, stormwater runoff and industries such as mining.

The ANZECC/ARMCANZ (2000) nickel default guideline value (DGV) for 95% species protection in marine water was a 'high reliability' value of 70 µg/L, based on chronic toxicity data for 15 species from five taxonomic groups, and the 99% species protection value of 7 µg/L was recommended for application to slightly-to-moderately disturbed ecosystems (ANZECC/ARMCANZ 2000). Since 2000, more toxicity data have become available, including data for tropical and temperate organisms and for Australian and/or New Zealand species, from which updated DGVs have been derived. The DGVs reported in this technical brief are based on the guideline values derived by Gissi et al. (2020).

DGVs for nickel in marine water were derived using chronic toxicity data for 24 temperate species and 16 tropical species (combined dataset of 40 species representing 15 taxonomic groups). The fit of the species sensitivity distribution (SSD) to the toxicity data was good, resulting in very high reliability DGVs. The DGVs for 99%, 95%, 90% and 80% species protection are 1.8 µg/L, 5.8 µg/L, 11 µg/L and 23 µg/L, respectively. The 95% species protection DGV is recommended for application to slightly-tomoderately disturbed ecosystems.

### 1 Introduction

Nickel is the fifth most common element on earth and occurs expansively in the earth's crust (Nickel Institute 2015). It primarily occurs as oxides, sulfides and silicates (Pyle and Couture 2012). Nickel ores are mined in over 23 countries and are smelted or refined in 25 countries, including Australia. Approximately 1.4 million tonnes of nickel are produced annually, and the world demand for nickel is growing at an average rate of 5% per annum (INSG 2016).

More than 75% of nickel produced is used in the production of alloys (e.g. stainless steel) with other metals such as iron, copper and chromium (INSG 2016). Nickel is used in food preparation equipment, mobile telephones, batteries, medical equipment, transport, buildings and power generation (Nickel Institute 2015). Anthropogenic sources of nickel include motor vehicle emissions, landfills, sewage, stormwater runoff and industries such as mining. Magmatic sulfide and laterite ores are naturally enriched in nickel. Nickel laterites have a fine dispersive nature and are formed by the extensive chemical and physical weathering of ultramafic rocks under tropical, humid conditions (Mudd 2010). In 2018, the US Geological Survey estimated that 60% of the world's nickel reserves were contained in laterite deposits and approximately 48% of global nickel production came from the tropical Asia–Pacific region (Gissi et al. 2020).

Nickel predominantly occurs in the +2 oxidation state (i.e.  $Ni<sup>2+</sup>$ ) and forms stable complexes with inorganic and organic ligands (Eisler 1998; Pyle and Couture 2012). In seawater, Ni<sup>2+</sup> is the main form of nickel (~36%), followed by chloride (27%) and carbonate (19%) species of nickel (Kumar 1986). Once nickel has entered an aquatic system, it can be accumulated by biota (e.g. phytoplankton, aquatic plants) or it can be deposited in the sediment by precipitation, complexation and adsorption on clay particles, with subsequent uptake in benthic biota (Cempel and Nikel 2006).

Concentrations of nickel in unimpacted marine coastal water using ultratrace sampling and analysis are typically <0.2 µg/L (Apte et al. 2018). Older data on background concentrations of nickel in seawater sampled in the North Pacific ranged from 0.15 µg/L to 0.66 µg/L (Bruland 1980). In Europe, Heijerick and Van Sprang (2008) reported 3.3 µg/L and 0.3 µg/L as the highest nickel concentrations for estuarine/coastal water and open ocean water, respectively. Van Geen and Luoma (1993) demonstrated that dissolved nickel concentrations increase closer to shore, with concentrations offshore of San Francisco Bay ranging from 0.26 µg/L to 0.32 µg/L and concentrations nearer to shore of ≤0.94 µg/L.

In some regions, such as New Caledonia, nickel concentrations in soils and aquatic systems are naturally enriched, but mining lateritic nickel ores can increase the input of metals into the coastal system. Dissolved nickel concentrations in New Caledonian seawater have been reported to range from <0.1 µg/L to 11 µg/L (Hedouin et al. 2009).

Nickel is an essential nutrient for micro-organisms and terrestrial plants, and at least eight nickelcontaining enzymes have been identified (Moreton et al. 2009). In aquatic plants and cyanobacteria, the necessity of nickel has been documented in urease and hydrogenase metabolism; however, its necessity in aquatic animals has not been confirmed (Muyssen et al. 2004).

The previous default guideline values (DGVs) for nickel were derived from chronic toxicity data for 15 species from five taxonomic groups (ANZECC/ARMCANZ 2000). The 99% and 95% species protection DGVs were 7 µg/L and 70 µg/L, respectively. The 99% species protection DGV was recommended for application to slightly-to-moderately disturbed marine systems because the 95% species protection value did not sufficiently protect: a group of species with acute toxicity values close to the 95% DGV; a juvenile mysid (152 µg/L (Gentile et al. 1982)); and unconfirmed data for a mollusc (61  $\mu$ g/L), a diatom (50–100  $\mu$ g/L) and two dinoflagellates (100  $\mu$ g/L).

Since the derivation of the ANZECC/ARMCANZ (2000) DGVs for nickel in marine water, DeForest and Schlekat (2013) derived a 5% hazardous concentration (HC5; analogous to a 95% species protection value) for nickel in marine water of 3.9 µg/L, largely influenced by data for the highly sensitive tropical sea urchin *Diadema antillarum* (EC10 of 2.9 µg/L), which is endemic to the Caribbean Sea (Bielmyer et al. 2005). If this species was excluded, the HC5 was 21 µg/L. DeForest and Schlekat (2013) recommended that *D. antillarum* be excluded from the temperate dataset for European waters because it was not endemic and because local urchin species were included.

Since 2000, more toxicity data for nickel in marine water have become available, including data for tropical, temperate and local species, from which updated DGVs have been derived. The DGVs reported here are based on the nickel marine guideline values derived by Gissi et al. (2020). They supersede the ANZECC/ARMCANZ (2000) DGVs for nickel in marine water.

## 2 Aquatic toxicology

### **2.1 Mechanism of toxicity**

Brix et al. (2017) provided a comprehensive review of the current understanding of the mechanisms of nickel toxicity to aquatic biota, although the focus was on freshwater organisms and some of the mechanisms may not be relevant to marine organisms. In marine and estuarine water, factors such as water chemistry and the physiology of estuarine and marine biota are expected to alter the mechanisms of toxicity and toxicological impact (Blewett and Leonard 2017). Mechanisms reported by Brix et al. (2017) include disruption of calcium, magnesium and iron homeostasis, induced oxidative damage via reactive oxygen species, and an allergic response of respiratory epithelia. The reduced calcium availability is known to affect exoskeleton, shell and bone growth in invertebrates (Brix et al. 2017). For aquatic plants, in addition to oxidative damage, high concentrations of nickel may displace magnesium from the chlorophyll molecule and inhibit photosynthesis (Brix et al. 2017).

Blewett and Leonard (2017) also reported ionoregulatory impairment, inhibition of respiration, and promotion of oxidative stress as the three main mechanisms of toxicity in marine invertebrates and fish. They concluded that, despite changes in the speciation of nickel in marine water, organism physiology appeared to be the key driver of toxic impact (Blewett and Leonard 2017).

Evidence of these effects on aquatic biota in chronic exposures at nickel concentrations found in the environment is limited. There has also been a lack of studies of diverse taxonomic groups and tropical species (Blewett and Leonard 2017). As such, the mechanisms of nickel toxicity in marine water are not well understood.

### **2.2 Toxicity**

Recently, the body of literature on the toxicity of nickel to marine species has increased, spanning over 40 species from over 15 taxonomic groups and representing temperate and tropical species. As reported in Section [4.1](#page-7-0) and by Gissi et al. (2020), there appears to be no difference in the toxicity of nickel between temperate and tropical species.

Echinoderm (sea urchin) early life stages were the most sensitive species to nickel. *Evichinus chloroticus* had a 96-h EC50 (larval abnormality) of 14 µg/L (Blewett et al. 2016), while *Diadema antillarum* had a 40-h EC10 (larval abnormality) of 2.9 µg/L (Deforest and Schlekat 2013). However, two species of echinoderm, *Dendraster excentricus* and *Strongylocentrotus purpuratus*, showed markedly lower sensitivity than other echinoderms, with 48-h EC10s (larval abnormality) of 191 µg/L and 335 µg/L, respectively. For sea urchin data, in two cases where both chronic EC50 and NOEC/EC10 values were available, factors of 5.2 and 5.0 were found for the EC50:NOEC/EC10 ratio, which supports the default conversion factor of 5 applied to chronic EC50 data to estimate negligible effect values as part of the Warne et al. (2018) derivation method.

Crustaceans and gastropods also showed high sensitivity to nickel. The tropical copepod *Acartia sinjiensis* was very sensitive, with an 80-h EC10 (development) of 5.5 µg/L (Gissi et al. 2018), while a 28-d NOEC (mortality) of 10 µg/L was reported for the mysid shrimp *Mysidopsis intii* (Hunt et al. 2002). Chronic EC10s or NOECs (for various endpoints and durations) of approximately 22–94 µg/L have been reported for the gastropods *Haliotis rufescens*, *Nassarius dorsatus* and *Monodonta labio* (Hunt et al. 2002; Gissi et al. 2018; Wang et al. 2019).

Bivalves and macroalgae appear to show intermediate sensitivity to nickel. Reported 48–96-h EC10/EC20s for bivalves range from approximately 90 µg/L to 430 µg/L, while 10 d EC10s for macroalgae range from approximately 100 µg/L to 150 µg/L. Algal species (including green algae, diatoms, cyanobacteria) are generally insensitive to nickel, with EC10/NOEC values ranging from 90 µg/L to 17 900 µg/L, while corals and fish are also amongst the least sensitive taxa, with EC10/NOEC values ranging from approximately 900 µg/L to 2 000 µg/L and from approximately 3 000 µg/L to 20 000 µg/L, respectively.

## 3 Factors affecting toxicity

The dissolved form of nickel, particularly the free cation  $Ni<sup>2+</sup>$ , is the most toxic form of nickel. Increased salinity lowers the concentration of Ni<sup>2+</sup> due to complexation with chloride (Byrne 2002). These changes in nickel speciation with differing pH and salinity affect its toxicity to aquatic organisms. Typically, toxicity decreases as salinity increases (Hall and Anderson 1995).

The water chemistry component most relevant to nickel bioavailability in marine water is dissolved organic carbon (DOC), as pH and cation content (salinity) do not vary substantially among marine sites. The effects of DOC on nickel toxicity are less clear for marine water than for freshwater. No clear influence of DOC was seen for the mussel *Mytilus galloprovincialis* for DOC in the range 1.2– 2.7 mg/L or for the diatom *Selenastrum costatum* in the range 0.2–2.7 mg/L (Deforest and Schlekat 2013). Blewett et al. (2016, 2018) showed that nickel toxicity to the urchin *E. chloroticus* and the mussel *Mytilus edulis* was influenced by both DOC quantity and quality. However, nickel toxicity varied by less than a factor of 2 among different natural water sources. Absorbance at 340 nm, which is indicative of the humic/fulvic content of the DOC, showed the strongest relationship with amelioration of nickel toxicity by DOC (Blewett et al. 2016, 2018). Due to the minimal effect DOC has been observed to have on nickel toxicity, no bioavailability normalisation approach has been recommended for the nickel DGVs in marine water.

## 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. Some additional details of the derivation are provided in Gissi et al. (2020).

### <span id="page-7-0"></span>**4.1 Toxicity data used in derivation**

A summary of the toxicity data and conversions used to derive the DGVs is i[n Table](#page-8-0) 1. Further details about the data and test conditions are in Appendix [A: Toxicity data that passed the screening and](#page-15-1)  quality assessment [and were used to derive the default guideline values.](#page-15-1) Details of the data quality assessment and the data that passed the quality assessment are provided as supporting information.

Due to the large size of the nickel toxicity dataset, it was initially divided into data for temperate species and data for tropical species. Temperate biota were defined as species isolated from temperate regions and/or having a natural geographical distribution outside of the Tropics of Cancer and Capricorn, and toxicity tests were conducted at temperatures <25°C. Tropical biota were defined as species that have a natural geographical distribution between the Tropic of Cancer and the Tropic of Capricorn, and toxicity tests were conducted at ≥25°C. Tests had measured salinity of ≥25 ppt, with the exception of one species (*Artemia salina*, which was conducted in seawater but salinity was not measured). Chronic toxicity data that passed the screening and quality assessment process were available for 24 temperate species from 10 taxonomic groups and for 16 tropical species from 10 taxonomic groups. A comprehensive comparison of the temperate and tropical datasets (Gissi et al. 2020) concluded the DGVs should be derived from the combined dataset of both temperate and tropical species. Briefly, the sensitivities of temperate and tropical marine species to nickel were similar, and species sensitivity distributions (SSDs) based on the temperate and tropical datasets resulted in protective concentrations (for 80%, 90%, 95% and 99% species protection) for temperate and tropical species that were not significantly different from each other (see Gissi et al. 2020). Therefore, there is no need for separate temperate and tropical DGVs for nickel in marine water. Moreover, combining the temperate and tropical datasets results in a larger dataset that includes more taxonomic groups (Gissi et al. 2020), which ultimately improves the confidence in the DGVs.

The combined dataset totalled 40 species from 15 taxonomic groups [\(Table](#page-8-0) 1). The toxicity data included chronic EC10, EC20, NOEC, LOEC and EC50 values. Although not required by the Warne et al. (2018) derivation method, the converted LOEC and EC50 data were included because they allowed a larger number and diversity of taxa to be represented. Chronic EC50s were divided by 5, and LOECs were divided by 2.5, to estimate chronic negligible effect (i.e. EC10, NOEC) values, as outlined by Warne et al. (2018). Where an EC50 and LOEC were available for the same species, the converted EC50 value was preferred. Where an EC10 and EC50 were available for the same species, only the EC10 value was used for the derivation.

Given the availability of many chronic toxicity data for a large number of taxonomic groups, acute data were not used in the derivation.

Measurements of DOC were not always reported in the original toxicity studies, but where reported were typically lower than 2.7 mg/L, where negligible amelioration of nickel toxicity would be expected.

In cases where both NOEC and EC10 data were available, professional judgement was used to select the most appropriate value. In making the decisions, the concentration–response relationships were closely examined to determine the toxicity value that best represented a negligible effect concentration. For the crustacean *Mysidopsis* intii, a NOEC of 10 µg/L for survival was chosen over an EC10 of 45.2 µg/L for growth (Hunt et al. 2002), and for the gastropod *Haliotis rufescens*, a NOEC of 21.5  $\mu$ g/L for shell growth was chosen over an EC10 of 36.4  $\mu$ g/L for metamorphosis (Hunt et al. 2002). For the brown-golden alga *Tisochrysis lutea*, a NOEC of 250 µg/L for 72-h growth rate was chosen over an E10 of 330 µg/L (Gissi 2018). In the case of the coral *Acropora digitifera,* an EC5 of 1 680 µg/L for 5-h fertilisation success was chosen over a NOEC of 940 µg/L (Gissi et al. 2017) as the concentration–response relationship suggested that the latter value would be too conservative.

An assessment of the modality of the final dataset confirmed that the dataset was not bimodal or multimodal (Appendix [B: Modality assessment for nickel](#page-22-1) toxicity to marine species).



<span id="page-8-0"></span>**Table 1 Summary of single chronic toxicity values, all species used to derive the default guideline values for nickel in marine water**





**a** Value is a geometric mean.

**b** Chronic EC50 value converted to a negligible effect (EC10/NOEC) concentration by dividing by a default conversion factor of 5.

**c** Chronic LOEC value converted to a negligible effect (EC10/NOEC) concentration by dividing by a default conversion factor of 2.5.

**d** EC10 from DeForest and Schlekat (2013) using data supplied by authors.

**e** Sensitive early life stage test defined as chronic.

### **4.2 Species sensitivity distribution**

The cumulative frequency (species sensitivity) distribution (SSD) of the chronic marine toxicity data for nickel reported in [Table](#page-8-0) 1 is shown in [Figure](#page-11-0) 1. The SSD was plotted using the Burrlioz 2.0 software. The model provides a good fit to the data [\(Figure](#page-11-0) 1).





Note: dotted line represents the extrapolation of the 95% species protection value for nickel: 5.8 µg/L.

#### <span id="page-11-0"></span>**Figure 1 Species sensitivity distribution, nickel in marine water**

### **4.3 Default guideline values**

It is important that the DGVs [\(Table](#page-12-0) 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](https://www.waterquality.gov.au/anz-guidelines) (ANZG 2018).

The DGVs for nickel in marine water for 99%, 95%, 90% and 80% species protection are provided in [Table](#page-12-0) 2. These supersede the ANZECC/ARMCANZ (2000) DGVs for nickel in marine water. The 95% DGV is protective of many species in the dataset; however, two echinoderms and one crustacean (copepod) were not protected—even though other species in these taxonomic groups were protected. The proportion of species not protected by the 95% DGV is expected for the size of the dataset. The 95% species protection DGV of 5.8 µg/L is recommended for application to slightly-tomoderately disturbed ecosystems.



### <span id="page-12-0"></span>**Table 2 Default guideline values, nickel in marine water, very high reliability**

**a** The DGVs were derived using the Burrlioz 2.0 software. They have been rounded to two significant figures.

### **4.4 Reliability classification**

The nickel 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—40 (preferred)
- type of toxicity data—chronic
- SSD model fit—good.

## **Glossary**



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



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

**Table A** 1 **Summary, chronic toxicity data that passed the screening and quality assurance processes, nickel in marine water – temperate species**

<span id="page-15-1"></span><span id="page-15-0"></span>







**a** EC10 from DeForest and Schlekat (2013) using data supplied by Hunt et al. (2002).

**b** Default conversion factor of 5 applied to chronic EC50 data to estimate negligible effect values as recommended by Warne et al. (2018).

### Table A 2 Summary, chronic toxicity data that passed the screening and quality assurance processes, nickel in marine water - tropical species

<span id="page-18-0"></span>







**a** Default conversion factor of 2.5 applied to chronic LOEC data to estimate negligible effect values as part of the Warne et al. (2018) derivation method.

**b** Intrinsic rate of increase: population growth = number of births – number of deaths.

**c** Default conversion factor of 5 applied to chronic EC50 data to estimate negligible effect values as part of the Warne et al. (2018) derivation method.

## <span id="page-22-1"></span>Appendix B: Modality assessment for nickel toxicity to marine species

A modality assessment was undertaken for the nickel in marine water toxicity dataset according to the four questions stipulated in Warne et al. (2018). These questions and their answers are as follows.

### **Is there a specific mode of action that could result in taxa-specific sensitivity?**

There are limited studies on the mechanism of nickel toxicity to marine organisms. Nickel possibly disrupts ion regulatory balance in invertebrates and could be a respiratory toxicant to fish. Nickel can also be a micronutrient for plants. It is likely that there are taxa-specific modes of action for nickel toxicity, although evidence is limited.

#### **Do the data suggest bimodality?**

Visual representation of the data, calculation of the bimodality coefficient (BC), and consideration of the range in the effect concentrations are recommended lines of evidence for evaluating whether bimodality or multimodality of the dataset is apparent. For this assessment:

- the histogram of the log10-tranformed nickel marine toxicity data [\(Figure](#page-22-0) B 1) indicates that the data are normally distributed and unimodal
- data that span large ranges (>4 orders of magnitude) indicate potential for underlying bimodality or multimodality (Warne et al. 2018); the nickel data span less than 4 orders of magnitude
- when the BC is greater than 0.555, it indicates that the data do not follow a typical normal distribution and may be bimodal; the BC for the log transformed data is 0.375 and, therefore, is not indicative of bimodality.

Based on the lines of evidence described above, the nickel marine toxicity dataset does not appear to be bimodal.



<span id="page-22-0"></span>**Figure B 1 Histogram, log10-transformed nickel marine toxicity data**

#### **Do the data show taxa-specific sensitivity?**

Nickel may exhibit taxa-specific toxicity, although it is difficult to make definitive conclusions. Generally, crustaceans ( $n = 10$ ), gastropods ( $n = 3$ ), echinoderms ( $n = 7$ ) and annelids (polychaetes)  $(n = 2)$  appear to be most sensitive to nickel, with bivalves  $(n = 4)$ , cnidaria  $(n = 3)$  and macroalgae (n = 2) exhibiting intermediate sensitivity, and fish (n = 3) and microalgae (n = 6) being least sensitive to nickel [\(Figure](#page-23-0) B 2). However, some of the taxa exhibit wide ranges in sensitivity, particularly the cnidarians, echinoderms, fish and microalgae, and many overlap in sensitivity [\(Figure](#page-23-0) B 2).



<span id="page-23-0"></span>

**Is it likely that indications of bimodality or multimodality or distinct clustering of taxa groups are not due to artefacts of data selection, small sample size, test procedures, or other reasons unrelated to a specific mode of action?**

It is not possible to determine if indications of taxa-specific sensitivity are real or due to artefacts. Regardless, the dataset displays no indications of bimodality or multimodality and, therefore, the full dataset was used for the derivation of the DGVs.

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