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Australian & New Zealand GUIDELINES FOR FRESH & MARINE WATER QUALITY

Toxicant default guideline values for aquatic ecosystem protection

Manganese in marine water

Technical brief

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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).

Manganese (Mn) is a widely distributed transition metal. It is sourced from natural geological erosion, emission and deposition processes, and discharges from municipal waste, industrial production and mining processes.

Background concentrations of manganese in coastal and ocean seawater range from 0.004 µg/L to 0.38 µg/L. Manganese in seawater exists as soluble Mn(II) and solid Mn(III/IV) oxides/oxyhydroxides. The dominant form of manganese in oxic surface waters is $Mn(H_2O)_6^{2+}$. The speciation of manganese is controlled primarily by redox potential, pH, sunlight, organic matter and microbial activity that can catalyse the redox processes.

Chronic effects of manganese on marine organisms are generally only detectable at concentrations above 1,000 µg/L, which is much higher than most environmental concentrations. However, the adult stage of some corals and embryos of some bivalve mollusc species are sensitive to lower concentrations. Reported toxicity values range between 500 µg/L and 1,000 µg/L. Acute toxicity values for tissue sloughing for adults of 3 coral species were the lowest in the dataset after being converted to estimated chronic-negligible-effect values using a coral-specific acute-to-chronic ratio of 2.3.

Moderate reliability DGVs for (dissolved) manganese in marine water were derived based on chronic-negligible-effect data and converted acute data for 18 species from 5 taxonomic groups with a good (visual) fit of the species sensitivity distribution to the toxicity data. The DGVs for 99%, 95%, 90% and 80% species protection are 190 µg/L, 300 µg/L, 390 µg/L and 570 µg/L, respectively. The 95% and 99% species-protection level DGVs protect the most sensitive species – corals. The 95% species-protection level DGV is recommended for adoption when assessing ecosystems that are slightly to moderately disturbed.

1 Introduction

Manganese (Mn) is a widely distributed transition metal and is the ninth-most abundant element in the Earth's bulk crust (Rudnick and Gao 2003). The most common ore minerals of manganese are oxides followed by carbonates and silicates (Maynard 2014). The world's largest manganese deposits are found as ferromanganese concretions, nodules and crusts located across the deep-sea floor and will be targeted for seabed mining in the future (Glasby 2006; Miller et al. 2018). Ninety percent of the manganese mined is used as an alloy with iron in steel production to improve hardness, stiffness and strength. It is also used in dry-cell batteries, paints, inks, glass, ceramics, fireworks and fertilisers (Summerfield 2021; WHO 2004). Manganese has been categorised as a critical mineral for Australia due to the growing demand for the metal in batteries for electric vehicles and many essential technologies (DISR 2023).

Important natural sources of manganese to the marine environment are volcanic emissions of particulates and aeolian dust deposition, erosion of manganese-containing rocks and soils, fluvial discharges, inundation of coastal acid-sulfate soils, deep-sea hydrothermal-vent emissions, and anaerobic zones of marine sediments where particulate manganese oxides are reduced (Van Hulten et al. 2017; WHO 2004). Anthropogenic sources of manganese include municipal wastewater discharges, wastes from coal and mineral mining and processing, emissions from steel and iron production, and combustion of fossil fuels (WHO 2004).

Background concentrations of dissolved manganese (operationally defined as the < 0.45-µm filtered fraction; Appendix A) are highest in the oxic surface layer of the open ocean and range from 0.004 µg/L to 0.160 µg/L (Appendix A). Dissolved manganese concentrations decrease to 0.005–0.008 µg/L in the deep ocean due to adsorption onto particles and the absence of light-associated reductive processes (dark oxidative processes lead to the formation of solid oxide phases) (Hansel 2017; Oldham et al. 2020; Van Hulten et al. 2017). Deep-sea hydrothermal vents can emit plumes of dissolved manganese at concentrations (0.27–103 µg/L) that are orders of magnitude greater than the surrounding background concentrations and extend several hundreds of kilometres from the source (Appendix A; Van Hulten et al. 2017). Shallower coastal waters can have higher background dissolved manganese concentrations (0.082–0.380 µg/L; Appendix A) than open oceans due to terrestrial influences. Concentrations in Australian east coast waters range from 1 µg/L to 10 µg/L (Jahan and Strezov 2017). In 6 Australian east coast ports with slight to moderate industrial activity, dissolved manganese concentrations ranged from 0.33 µg/L to 101 µg/L (Appendix A). In the case of the 2015 collapse of the Fundão tailings dam in Brazil, the average dissolved manganese concentration measured in the downstream Rio Doce estuary in 2017 was 582 µg/L ± 626 µg/L (Queiroz et al. 2021).

Marine sediment porewaters can have very high natural dissolved manganese concentrations (443–11,000 µg/L; Appendix A). Where anoxic conditions exist at the sediment–water interface, dissolved manganese fluxes from the reduction of manganese dioxide (MnO_2) in marine sediments can generate elevated dissolved concentrations (e.g. 7.7–440 µg/L) in the overlying water (Appendix A).

The dominant cationic oxidation states of manganese in seawater are: Mn(II) (dissolved, $Mn(H_2O)_6^{2+}$), Mn(III) (dissolved ligand complexes and solid and colloidal III/IV oxides) and Mn(IV) (solid and

colloidal, MnO_2) (Oldham et al. 2017; Oldham et al. 2020; Tebo et al. 2004). While most dissolved manganese in seawater is Mn(II), primarily as $Mn(H_2O)_6^{2+}$, complexes with chloride, sulfate, bicarbonate and organic ligands can also exist. Recent evidence showed that Mn(III)-ligand complexes can remain stable and dominate the dissolved phase. However, in the absence of ligands, Mn(III) undergoes rapid disproportionation to dissolved Mn(II) and solid Mn(IV) phases (Hansel 2017; Oldham et al. 2017). Colloidal (> 1 kDa and < 0.45 µm) forms of MnO_2 are likely to be present as thin surface coatings but, unlike freshwater and estuarine environments, there is little evidence for a marked contribution of colloids to dissolved manganese concentrations in seawater (Fang and Wang 2022). Solid-phase manganese oxides are strong oxidants and can oxidise dissolved Mn(II). They also have high sorptive capacities for metals and radionuclides and, hence, play an important role in the biogeochemical cycles of elements such as carbon, oxygen, sulfur, iron, arsenic, copper, cobalt, cadmium, nickel, lead and zinc (Tebo et al. 2004). Manganese and iron are strongly associated. Both Mn(III) and Mn(IV) are prevalent in ferromanganese (oxyhydr)oxide forms (Tebo et al. 2004).

Redox conditions, pH, sunlight, organic matter and microbial activity largely control the environmental chemistry of manganese in seawater. Manganese(II) dominates at low pH and redox potentials (WHO 2004). Although Mn(III/IV) oxides are the thermodynamically favoured forms in oxic surface waters, reduced Mn(II) dominates manganese speciation due to the extremely slow kinetics of oxidation coupled with the rapid photoreduction of Mn(IV) oxides (Bruland et al. 1994; Hansel 2017; Sunda and Huntsman 1994). The oxidation of dissolved Mn(II) to solid Mn(IV) oxides by abiotic processes is extremely slow – the half-life is 500 years (Sunda 2012) – but can be accelerated to a half-life of mere hours by microbial activity (Learman et al. 2011; Tebo et al. 2004). Manganese-oxidising bacteria can catalyse the reaction by direct (secretion of enzymes) and indirect (modification of local pH or redox conditions) processes (Tebo et al. 2004). Conversely, manganese-reducing bacteria catalyse the dissolution of settled solid Mn(IV) oxides to create a flux of dissolved Mn(II) released from sediments to the overlying water (Hansel 2017; Tebo et al. 2004). Sunlight is thought to slow the rate of Mn(II) oxidation by inhibiting microbial activity and increasing the reductive dissolution of solid Mn(IV) oxides by excitation of organic matter adsorbed to the oxide surface (Waite and Szymczak 2018). Reactive oxygen species (ROS) produced photochemically or biotically influence the oxidation state of manganese by oxidising Mn(II) and reducing MnO_2 (Oldham et al. 2020). Manganese and iron redox cycles are closely coupled, as they co-exist in various forms and each influences the solubility and, hence, bioavailability of the other (Liu et al. 2022). Sulfides can also play a role in reducing MnO_2 (Hansel 2017).

Internationally, very few formal guideline values exist for manganese in marine water. ANZECC and ARMCANZ (2000) were unable to derive a default guideline value (DGV) for manganese in marine water due to insufficient data and, instead, recommended a low-reliability interim working level based on acute and chronic toxicity data for 5 species from 3 taxonomic groups, comprising values for one crustacean (acute toxicity), 2 bivalve molluscs (acute toxicity) and 2 diatoms (chronic toxicity). The lowest toxicity value was for the Eastern oyster *Crassostrea virginica* (48-hour LC50 [see 'Glossary and acronyms' for definitions] of 16,000 µg/L; Calabrese et al. 1973), which was divided by an assessment factor of 200 (for an essential metal) to give a low-reliability interim working level of 80 µg/L for marine water. A 95% species-protection level marine manganese guideline value of 300 µg/L was derived by WHO (2004) using a species sensitivity distribution (SSD) that combined acute and chronic data and applied assessment factors of 5 or 10 to chronic EC50 or acute LC50 values, respectively, to estimate chronic no-observed-effect concentrations (NOECs). Levy et al.

(2004) derived a site-specific guideline value of 660 µg/L using toxicity data reported by WHO (2004) and data from 5 Australian species (3 chronic NOEC values and 2 acute NOEC values that were converted to estimated chronic values using an acute-to-chronic ratio [ACR] of 3.1). Stauber (2006) combined the WHO (2004) and Levy et al. (2004) data (using an ACR of 12.4 instead of 3.1), as well as data for a sensitive coral species (Stauber et al. 2002), to derive a site-specific manganese guideline value of 140 µg/L at the 95% species-protection level. The guideline values derived by WHO (2004), Levy et al. (2004) and Stauber (2006) are 2 to 8 times higher than the ANZECC and ARMCANZ (2000) interim working level, suggesting that the interim working level is overly conservative. The DGVs reported here build upon the previous guideline value derivations and supersede the ANZECC and ARMCANZ (2000) interim working-level value.

2 Aquatic toxicology

2.1 Mechanisms of toxicity

Manganese is an essential element for all organisms and is involved in many biochemical pathways and physiological functions. Manganese can be toxic when present at concentrations that exceed essential requirements, although the mechanisms of manganese toxicity are not well understood (Hernroth et al. 2020; Roth et al. 2013).

Molecular studies on the biochemical pathways in aquatic organisms that are affected by excess manganese are lacking; however, some of these pathways are evolutionarily conserved and can be extrapolated between organisms. Manganese(II) (and, in some cases, Mn(III)) is a co-factor in many enzymes, such as the tetra-Mn cluster present in the reaction-centre complex of photosystem II for photosynthesis, the antioxidant superoxide dismutase present in mitochondria for preventing damage by ROS, and glutamine synthetase involved in controlling the neurotransmitter glutamate (Baden and Eriksson 2006; Hansel 2017). Cellular Mn(II) uptake is highly regulated through general divalent cation membrane transporters that are also used by calcium and iron. Cellular uptake is also regulated by specific homeostatic proteins. Manganese is accumulated in the nucleus, mitochondria and Golgi apparatus at a cellular level and in the brain, neurons, liver, hepatopancreas, gills, blood and skeleton at a whole-organism level (Baden and Eriksson 2006; Hernroth et al. 2020; Martinez-Finley et al. 2013).

Due to the low toxicity of manganese, experimental studies on its mechanisms of toxicity have been performed at very high concentrations that would not occur in the environment. Nevertheless, they provide useful indications of where mechanistic investigations can be targeted in the future. Excessive exposure to manganese disrupts the electron transport chain in mitochondria, resulting in a decrease in ATP (adenosine triphosphate) and an increase in ROS, which can lead to oxidative stress and cell apoptosis (Hernroth et al. 2020; Kim et al. 2013; Martinez-Finley et al. 2013). As well as causing oxidative stress, excess manganese can impair calcium homeostasis and result in skeletal deformities. For example, at 68 hours post-fertilisation, sea urchin embryos exposed to manganese (61,500 µg/L) did not develop endoskeletons due to manganese preventing the uptake of calcium by skeletogenic cells (Pinsino et al. 2011). Excess manganese may also cause dysfunctionalities of immunocytes and increased susceptibility to infections (Hernroth et al. 2020). Immune suppression was measured in the Norway lobster (*Nephrops norvegicus*) when exposed to 20,000 µg/L for 10 days, which caused a 44% reduction in haemocytes due to cell apoptosis (Oweson et al. 2006). Although no mechanistic studies are available for marine fish, studies exposing freshwater fish to manganese have shown that manganese disrupts carbohydrate metabolism, haematological parameters, and sodium and calcium metabolism, ultimately leading to oxygen deprivation (WHO 2004). Manganese is a well-known neurotoxin causing Parkinson's-like symptoms known as manganism in humans (Martinez-Finley et al. 2013). Neurotoxicity caused a neuromuscular disturbance in adult sea stars (*Asterias rubens*) and brittle stars (*Ophiocomina nigra*) that impaired their capacity to turn over following a 14-day exposure to 12,000 µg/L (Sköld et al. 2015). Similar neurotoxic effects were observed in Eastern oysters. The beating rates of oyster gill cilia reduced following a 3-day exposure to 55,000 µg/L due to the disruption of the dopaminergic, cilio-inhibitory system (Martin et al. 2008).

In summary, oxidative stress, disruption of homeostasis, immunosuppression and neurotoxicity are some of the proposed mechanisms of manganese toxicity.

2.2 Toxicity

Due to manganese being essential for many biochemical processes and physiological functions, organisms are able to regulate excess internal concentrations to a certain threshold before toxicity occurs. Accumulation of manganese varies widely between species and has been reported as ranging from < 0.2 mg/kg to 3,100 mg/kg (although a large fraction of the manganese in crustaceans is associated with the carapace and does not result in toxicity). Bioconcentration factors range from 35 to 20,000 (Iyagbaye et al. 2022a; WHO 2004). There is no evidence of manganese biomagnification in marine ecosystems – fish accumulate lower concentrations of manganese than algae and invertebrates (WHO 2004). In contrast, manganese deficiencies have been reported for marine phytoplankton and fish when given manganese-free diets. This resulted in reduced growth (Browning et al. 2021) and skeletal deformation (Lall and Kaushik 2021), respectively. Half-lives of manganese in marine organism tissues were measured to be 1.8–36 days, depending on dietary or aqueous exposure routes (WHO 2004).

The toxicity of excess manganese at the whole-organism level is generally only detectable at concentrations above 1,000 µg/L, which is much greater than most environmental concentrations. The exceptions are adults of some coral species (*Acropora spathulata, Acropora muricata* and *Stylophora pistillata*) that had acute 48-hour EC50 values of 700–933 µg/L for effects on tissue sloughing (Stauber et al. 2002; Summer et al. 2019; Binet et al. 2023) (see Appendix B for a summary of manganese toxicity data for coral species). Tissue sloughing is when coral tissue peels away from the skeleton without bleaching, i.e. without the loss of the symbiotic dinoflagellate *Symbiodinium* spp. (Binet et al. 2023). Stauber et al. (2002) found no effects on isolated *Symbiodinium* spp. density or photosynthetic yield at 1,000 µg/L; however, 50% tissue sloughing occurred in the host coral *S. pistillata* at 860 µg/L. As the area of tissue sloughing increases, a point is reached where the coral does not recover and eventually dies. The sensitivity to manganese based on the biological endpoint of tissue sloughing varied between coral species. Adult *Acropora millepora* were 3–4 times less sensitive than adults of other coral species (Golding et al. 2023). Early life stages are also less sensitive than adults. Acute larval mortality effect concentrations range from 4,000 µg/L to 36,000 µg/L (Summer et al. 2019). Chronic fertilisation endpoints in 2 coral species (*A. spathulata* and *Platygyra daedalea*) were also markedly less sensitive than acute adult tissue sloughing – effect concentrations ranged from 15,000 µg/L to 237,000 µg/L (Summer et al. 2019). The only 14-day chronic NOEC value (> 1,090 µg/L) for adult coral tissue sloughing was for the least sensitive *A. millepora* coral, where no tissue sloughing was observed at manganese concentrations up to and including the highest exposure concentration of 1,090 µg/L (Golding et al. 2023). Binet et al. (2023) and Summer et al. (2019) hypothesised that oxidative stress (using indicators other than superoxide dismutase, which was not responsive), immunosuppression, calcium interference and excess mucous production could all contribute to the mechanisms of tissue sloughing observed in adult corals after acute exposures to manganese. Low-level enrichment of dissolved manganese (4 µg/L) was beneficial for *S. pistillata* adults by increasing resistance to heat-stress-induced bleaching (Biscéré et al. 2018; Montalbetti et al. 2021). Therefore, further research is needed on adults of coral species to determine chronic tissue-sloughing effect concentrations and mechanisms of toxicity. In the absence

of this knowledge, estimated chronic effects derived by dividing acute EC50 values by the ACR can be used to provide adequate protection for these sensitive species.

Anemones and jellyfish are in the same phylum as coral (i.e. Cnidaria) but are not as sensitive as adult corals to dissolved manganese. Acute and chronic effect concentrations range from 46,200 µg/L to 354,000 µg/L and from 41,800 µg/L to 103,000 µg/L, respectively (Anastasi 2014; Iyagbaye et al. 2022a; Iyagbaye et al. 2022b; Summer et al. 2019). Iyagbaye et al. (2022a) reported a 24-day LOEC of 460 µg/L for tentacle retraction in the anemone *Exaiptasia pallida.* Partial recovery was observed after 6 days in uncontaminated seawater. Recovery following 6 days' depuration was also observed for anemones exposed to 100 mg/L manganese, indicating that manganese had a temporary influence without significant long-term effects (Iyagbaye et al. 2022a).

As mentioned previously, symbiotic dinoflagellates (i.e. *Symbiodinium* spp.) of corals and anemones are highly tolerant to exposure to dissolved manganese (Binet et al. 2023; Iyagbaye et al. 2022a; Stauber et al. 2002). Other microalgae (including diatoms) are similarly tolerant – EC50 values range from 1,500 µg/L to 390,000 µg/L (Canterford and Canterford 1980; ESA 2008). Manganese also ameliorates the toxicity of copper to the marine diatom *Ceratoneis closterium* (formerly known as *Nitzschia closterium*) by binding the copper to Mn(III) hydroxides formed on the algal membrane surface (Stauber and Florence 1985). Similarly, manganese reduces the toxicity or uptake of cadmium and zinc by green microalgae and diatoms, demonstrating the role that manganese plays in metal regulation in phytoplankton (Sunda and Huntsman 1998). The macroalga *Ulva pertusa* had acute 96-hour EC50 values ranging from 1,430 µg/L to 2,710 µg/L for spore release (Han et al. 2009).

Invertebrates other than cnidarians exhibit a broad range of sensitivities to dissolved manganese. Acute EC50 values and chronic EC50 values range from 7,700 µg/L to > 300,000 µg/L and from 2,700 µg/L to 681,000 µg/L, respectively (Anastasi 2014; Eisler 1977; ESA 2008; Levy et al. 2004; Markich 2021). Bivalves are more sensitive than most other invertebrates. Chronic NEC values and chronic EC50 values for embryo larval development range from 650 µg/L to 2,410 µg/L and from 2,700 µg/L to 9,800 µg /L, respectively (Markich 2021). Only acute toxicity data were available for crustaceans – effect concentrations ranged from 600 µg/L to 178,000 µg/L (Anastasi 2014; Frías-Espericueta et al. 2003). An exception to this was the chronic 7-day embryo mortality and hatching success of the brachyuran crab *Cancer anthonyi*, where a nominal 10 µg/L resulted in 27% mortality and a 38% reduction in hatching success (Macdonald et al. 1988). However, the data for this species was considered unreliable (see Section 4.1). Sea urchin toxicity values ranged from 137 µg/L to 681,000 µg/L for acute effects on sperm motility (based on nominal manganese concentration) and chronic effects on fertilisation (ESA 2008; Young and Nelson 1974). Mortality effects on a polychaete (*Diopatra aciculata*) from 10-day dissolved manganese exposure, relevant to sediment porewater exposure, resulted in LC10 and LC50 values of 70,500 µg/L and 165,000 µg/L, respectively, demonstrating the high tolerance of benthic marine organisms to manganese (Anastasi 2014). Smothering effects of precipitated Mn(III/IV) oxides have not been investigated; however, a black layer of precipitated manganese on the gills of the Norway lobster was observed in the field, although the effects on respiration were unknown (Baden and Eriksson 2006).

Acute toxicity of dissolved manganese to marine fish ranged from a 96-hour LC50 of 12,200 µg/L for juvenile grouper (*Epinephelus* sp.) (Wang et al. 2022a) to a 96-hour EC50 of > 1,000,000 µg/L for imbalance of larval barramundi (*Lates calcarifer*) (ESA 2008). There were no chronic toxicity values

for marine fish, but under estuarine conditions of 15 practical salinity units (PSU), juvenile Guinean tilapia (*Tilapia guineesis*) had a 28-day NOEC of 2,300 µg/L for effects on growth (Oyewo and Don-Pedro 2006). Chronic 30-day exposure of juvenile *Epinephelus* sp. to 500–4,000 µg/L in seawater (28–29 PSU) resulted in upregulation of antioxidant and apoptosis genes and increased liver damage, which were all indicative of oxidative stress (Wang et al. 2022b).

Acute and chronic manganese toxicity values specific to Australian or New Zealand marine species ranged from 50 µg/L to > 1,000,000 µg/L and can be found for green and golden microalgae, diatoms, dinoflagellates, macroalgae, corals, anemones, jellyfish, annelids, crustaceans, bivalves, sea urchins and fish (Anastasi 2014; Bengtsson 1978; Binet et al. 2023; Iyagbaye et al. 2022a; Iyagbaye et al. 2022b; Levy et al. 2004; Markich 2021; Stauber et al. 2002; Summer et al. 2019).

3 Factors affecting toxicity

The solubility of manganese is one of the main factors affecting its toxicity. Dissolved Mn(II) as $Mn(H_2O)_6^{2+}$ is the most bioavailable and, therefore, the most toxic form. Colloidal Mn(III/IV) and solid MnO_2 are much less toxic (WHO 2004). The ranking of the solubilities of manganese compounds from most to least soluble in water is: Mn(II) nitrate, Mn(II) acetate, Mn(II) chloride, Mn(II) sulfate, Mn(II) fluoride, Mn(VII) oxide. In contrast, Mn(II) carbonate, Mn(II) sulfide, Mn(II) hydroxide and Mn(IV) oxides are poorly soluble or insoluble (Aylward and Findlay 2008). Most toxicity data are based on soluble Mn(II) chloride or Mn(II) sulfate. The only study to test the toxicity of different oxidation states in seawater compared the effects of Mn(II) chloride, Mn(VII) potassium permanganate and insoluble Mn(IV) dioxide on the 48-hour hatching success of a brine shrimp (*Artemia salina*) in natural seawater (31 PSU) (Liu and Chen 1987). The most toxic form was Mn(VII), which is a strong oxidising agent and unstable in seawater, so would only be relevant for permanganate discharges (Peters et al. 2012). This was followed by Mn(IV), where precipitation at ≥ 10,000 µg/L confounded dissolved manganese toxicity, and Mn(II). However, all responses were based on nominal concentrations, compromising the reliability of the data (Liu and Chen 1987). The bioavailability of 4 different dietary forms of manganese (Mn(II) chloride, Mn(II) sulfate, Mn(II) carbonate and Mn(IV) dioxide) given to a freshwater fish for 20 weeks differed markedly. The 2 poorly soluble forms (Mn(II) carbonate and Mn(IV) dioxide) caused dwarfism as a result of manganese deficiency, demonstrating that solubility also influences dietary uptake and potential toxicity of manganese (Satoh et al. 1987).

As mentioned previously, physicochemical parameters that influence manganese speciation, solubility, bioavailability and potential toxicity are redox potential, pH, temperature, microbial activity, sunlight and organic matter (by increasing microbial activity) (WHO 2004). There is little evidence for dissolved organic carbon forming strongly bound complexes with manganese that could reduce its bioavailability (Markich 2021; Peters et al. 2011; WHO 2004). The effect of salinity or pH on manganese toxicity has not been specifically investigated. Toxicity values for freshwater biota are also generally > 1,000 µg/L (with some exceptions documented in Harford et al. 2015 and Peters et al. 2012), suggesting there are no major differences in toxicity between marine and freshwater biota. However, as high water hardness is known to reduce manganese toxicity in freshwater (ANZG 2018; Peters et al. 2011; WHO 2004), manganese toxicity in seawater could be lower than in most freshwaters. Manganese toxicity values for estuarine organisms are also generally > 1,000 µg/L. For example, chronic exposure of the Guinean tilapia (28-day growth) and gastropod mollusc *Tympanotonus fuscatus* (28-day growth) to manganese in estuarine waters (15 PSU) resulted in NOEC values of 2,300 µg/L and 8,410 µg/L, respectively (Oyewo and Don-Pedro 2006). Therefore, DGVs for manganese in marine water may also protect estuarine ecosystems; however, site-specific guideline values are preferable. With regards to the application of the DGVs to estuarine waters, ANZG (2018) advises that the DGVs for marine water are considered more relevant to estuarine water bodies that are higher in salinity, but where the salinity of a water body changes frequently, the lowest of the marine and freshwater DGVs should be used.

4 Default guideline value derivation

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

4.1 Toxicity data used in derivation

A total of 192 acute and chronic toxicity values for manganese were scored using the quality-assessment criteria, resulting in 4% of the data being of unacceptable quality (scoring < 50%) and 96% being of acceptable quality (scoring ≥ 50%). Forty-four per cent of the data was of high quality (scoring ≥ 80%). Of the toxicity values that scored ≥ 50%, 105 were acute and represented 24 species, while 79 were chronic and represented 29 species. The acceptable-quality data were screened further to remove all acute values, given that there were sufficient preferred chronic values to meet the minimum data requirements, and to remove those values based on nominal manganese concentrations. The exceptions to this were the acute adult coral tissue-sloughing toxicity values, one of which was based on nominal manganese concentrations, as discussed below.

The acute coral values were retained because the adult tissue-sloughing endpoint was the most sensitive manganese toxicity endpoint for corals (Appendix B) and was more sensitive than most chronic endpoints for marine biota recorded in the literature thus far. Corals are of high ecological and economic significance to Australia (e.g. Ningaloo Reef and the Great Barrier Reef) and New Zealand (deep-sea and sub-tropical corals) and they are protected under statutory requirements and international agreements (e.g. World Heritage Convention and the Convention on International Trade in Endangered Species). The only chronic value for adult tissue sloughing was for *A. millepora*, a species found to be 3–4 times more tolerant to acute manganese exposure than the 3 other coral species for which there were acute data, based on EC50 values (Appendix B). Therefore, it was necessary to include the acute data for these more sensitive corals to ensure the protection of corals generally and the reef ecosystem they support. The quality-assessment scores for the toxicity values that formed the coral dataset ranged from 65% to 98%.

Data for the coral *S. pistillata* were from a confidential report by Stauber et al. (2002) that is not publicly available. In accordance with Warne et al. (2018), the data for this species were reviewed by an independent assessor with expertise in DGV derivation. The independent assessment found the acute EC50 (tissue sloughing) and LC50 values for *S. pistillata* to be of acceptable quality. Scores were 71% and 76%, respectively. These values were consistent with the 66% and 70% scores calculated during the initial data-assessment and screening stage. Notably, the data for this species did not meet the quality-assessment condition requiring confirmation that test-acceptability criteria were stated or inferred (e.g. by citing well-established protocols, such as ASTM). However, as the toxicity values passed the overall quality assessment and there was other evidence of due diligence in the study (e.g. the use of negative controls and additional handling controls, both of which had 100% survival), the data were included in the derivation.

The acute 48-hour EC50 tissue-sloughing toxicity values for adults of the 3 coral species *A. muricata*, *A. spathulata* and *S. pistillata* were converted to estimated chronic values by dividing the EC50 by a coral-specific ACR of 2.3. The coral-specific ACR was calculated by dividing the acute 48-hour EC50

(2,560 µg/L) for adult *A. millepora* by the chronic 14-day NOEC for adult *A. millepora* (≥ 1,090 µg/L, used as 1,090 µg/L (Golding et al. 2023)).

A chronic NOEC value for fertilisation was used for the coral *P. daedalea* rather than a lower available EC10 value, as the reliability of the EC10 value was low, according to Summer et al. (2019) (Appendix B and Appendix C).

The chronic 24-day LOEC of 460 µg/L for tentacle retraction in the anemone *E. pallida* (Iyagbaye et al. 2022a) based on measured dissolved manganese was not included in the final toxicity dataset because (i) there were sufficient chronic NEC and NOEC values that met the minimum data requirements, (ii) additional uncertainty would have been added to the LOEC value for the anemone by applying the recommended conversion factor of 2.5, which would have resulted in an estimated chronic value lower than the lowest test concentration, and (iii) the anemones were capable of recovering from tentacle retraction when placed in clean seawater. Iyagbaye et al. (2022a) suggested that the recovery implied that longer-term detrimental effects of low-exposure concentrations would be negligible.

The only chronic toxicity data available for crustaceans (for *C. anthonyi*, from Macdonald et al. 1988) were not included in the final toxicity dataset because they did not meet the data requirements as specified by Warne et al. (2018), in that (i) the toxicity data were based on nominal rather than measured manganese concentrations, (ii) the dose responses were non-monotonic and part of a 10-fold dilution series, and (iii) preferred negligible effect concentrations (i.e. NEC, EC/LC10, NOEC) were not derived. Only data that achieved a quality score of ≥ 70% (considered acceptable to high quality in accordance with Warne et al. 2018) were included in the dataset. The data for *C. anthonyi* was assigned an overall quality score of 67%.

There was concern that the inclusion of 10 bivalve mollusc species from Markich (2021) in the dataset might result in an over-representation of this taxonomic group (i.e. 56% of the final dataset being bivalves). The chronic NEC values for these bivalves ranged from 650 µg/L to 2,410 µg/L and encompassed the median, upper and lower quartile of the SSD dataset. The influence that these bivalve data had on the SSD and associated protective concentration (PC) values was assessed (Appendix D). The inclusion of the bivalve data increased the sample size (from 8 to 18) and taxonomic representation (from 4 to 5 taxonomic groups) and improved the fit of the SSD but did not change the reliability of the resulting PC values. The additional data also resulted in the DGVs increasing by a factor of 1.2–2.4. The assessment provided no strong argument to exclude the Markich (2021) bivalve data. Consequently, the Markich (2021) data were included in the final dataset used to derive the DGVs.

All data except for the 48-hour EC50 value for tissue sloughing by adults of one coral species (*A. spathulata*) were based on measured manganese. The toxicity values for the sea urchin, diatom and microalga from ESA (2008) and Levy et al. (2004) were based on measured manganese in the highest concentration and nominal concentrations for the remaining dilution series that were calculated from the measured concentration. While this approach is not preferred, these data were included in the final dataset because a one-point validation of the highest manganese concentration was made and there was nothing in the concentration-response data (such as an interrupted or non-monotonic response) to suggest that the dilution series using the highest validated concentration

had been prepared incorrectly. Toxicity values for most of the corals and all bivalves were based on < 0.45-µm filtered manganese. Filtration was not stipulated for the measured manganese in the sea urchin and microalgae tests; however, Levy et al. (2004) showed no difference between nominal and measured manganese up to 98,000 µg/L. Therefore, it is likely there is minimal difference between filtered and unfiltered manganese concentrations in seawater up to 98,000 µg/L.

Given the above considerations, the final dataset used for the derivation of the DGVs for dissolved manganese in marine water included chronic toxicity data for 18 species from 5 taxonomic groups comprising 5 cnidarians (corals), 10 bivalve molluscs, one echinoderm (sea urchin), one diatom and one golden microalga. The dataset included 3 estimated chronic values, 5 chronic NOEC values and 10 chronic NEC values. An assessment of the modality of the final dataset indicated that it was likely to be unimodal and that the full dataset could be used to derive the DGVs (Appendix E). Quality-assessment scores for the 18 toxicity values used to derive the DGVs ranged from 70% to 96%. All 18 final toxicity values were based on toxicity testing using manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$). The temperature, pH and salinity of test solutions ranged from 20–27 °C, 7.0–8.3 pH units and 25–37 PSU, respectively (Appendix C). Toxicity values were not adjusted for any water-quality parameters. Table 1 summarises the toxicity data (consolidated to one value per species) used to derive the DGVs for manganese in marine water. Appendix C lists further details for all the data used to derive the DGVs and associated test conditions. Details of the data-quality assessment and the data that passed the quality assessment are provided as supporting information.

Commented [RvD1]: *Note to DCCEEW web team:* Add hyperlink to data quality assessment spreadsheet once url known.

Commented [RvD2]: *Note to DCCEEW web team:* Add hyperlink to data entry spreadsheet once url known.

Table 1 Summary of chronic and converted acute toxicity values used to derive the default guideline values for manganese in marine water

Taxonomic group	Species	Life stage	Duration (hours)	Type (acute/ chronic)	Toxicity measure (endpoint)	Final toxicity value (µg/L)
Diatom	*Ceratoneis closterium*[a]	N.A.	72	Chronic	NOEC (growth rate)	18,000
Golden microalga	*Tisochrysis lutea*[b]	Log phase	72	Chronic	NOEC (growth rate)	125,000
Cnidarian (coral)	*Acropora millepora*	Adult	336	Chronic	NOEC (tissue sloughing)	1,090
	Acropora muricata	Adult	48	Acute	EC50 (tissue sloughing)	358[c,d]
	Acropora spathulata	Adult	48	Acute	EC50 (tissue sloughing)	304[c]
	Platygyra daedalea	Gametes	5.5	Chronic	NOEC (fertilisation)	54,000
	Stylophora pistillata	Adult	48	Acute	EC50 (tissue sloughing)	374[c]
Echinoderm (sea urchin)	*Heliocidaris tuberculata*	Embryo	72	Chronic	NOEC (embryo development)	1,580[d]
Mollusc (bivalve)	*Anadara trapezia*	Embryo	48	Chronic	NEC (embryo development)	1,040
	Barnea australasiae	Embryo	48	Chronic	NEC (embryo development)	1,780
	Fulvia tenuicostata	Embryo	48	Chronic	NEC (embryo development)	1,460
	Hiatula alba	Embryo	48	Chronic	NEC (embryo development)	1,520
	Irus crenatus	Embryo	48	Chronic	NEC (embryo development)	2,410
	Magallana gigas[e]	Embryo	48	Chronic	NEC (embryo development)	650
	Saccostrea glomerata[f]	Embryo	48	Chronic	NEC (embryo development)	654
	Scaeochlamys livida	Embryo	48	Chronic	NEC (embryo development)	959
	Spisula trigonella	Embryo	48	Chronic	NEC (embryo development)	2,090
	Xenostrobus securis	Embryo	48	Chronic	NEC (embryo development)	755

Values are reported to no more than 3 significant figures.
[a] Formerly known as *Nitzschia closterium.*
[b] Formerly known as *Isochrysis galbana*.
[c] Estimated chronic toxicity value derived by dividing the acute EC50 by a coral-specific acute-to-chronic ratio of 2.3.
[d] Geometric mean of several values. See Appendix C for details.
[e] Formerly known as *Crassostrea gigas.*
[f] Formerly known as *Saccostrea commercialis.*

4.2 Species sensitivity distribution

Figure 1 shows the SSD of the 18 chronic and acute (converted to chronic) marine manganese toxicity values reported in Table 1. The fit of the SSD based on visual assessment was good, especially at the mid-to-lower end of the curve. Burrlioz 2.0 fitted an inverse Weibull model through the 18 data points.

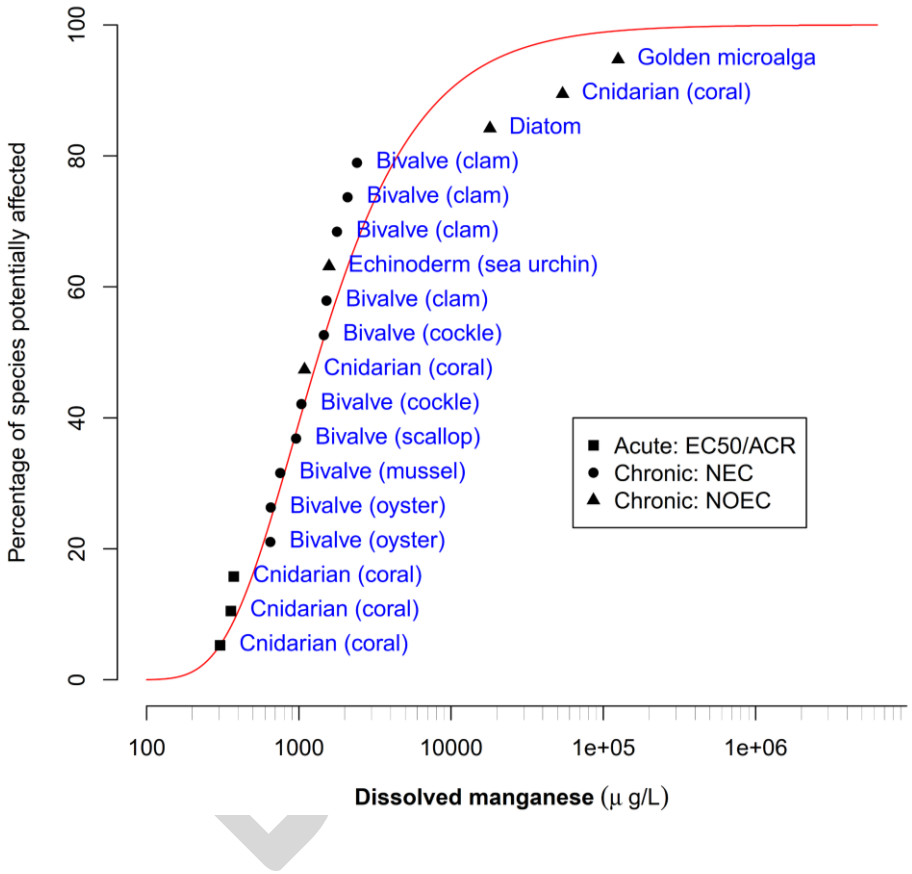

Figure 1 Species sensitivity distribution for dissolved manganese in marine water

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 for manganese in marine water. The DGVs relate to dissolved manganese, operationally defined as the < 0.45-µm filtered measurement. The 95% species protection DGV is recommended when assessing marine ecosystems that are slightly to moderately disturbed. The DGVs are based on toxicity data generated at pH 7.0–8.3 and salinity 25–37 PSU, where reported.

Table 2 Toxicant default guideline values for dissolved manganese in marine water with moderate reliability

Level of species protection (%)	DGV for dissolved manganese in marine water (µg/L)[a]
99	190
95	300
90	390
80	570

[a] The DGVs were derived using the Burrlioz 2.0 software and have been rounded to 2 significant figures.

The 95% species-protection DGV of 300 µg/L is very similar to the most sensitive toxicity value of 304 µg/L for adults of the coral *A. spathulata* and is very likely to be protective, given that the coral value is estimated from an acute EC50 value. The 95% species-protection DGV is also 3.6 times lower than the only unconverted chronic toxicity data for adults of the coral (*A. millepora* tissue sloughing), further supporting that the DGVs will provide protection for corals.

The DGVs are well above background concentrations of dissolved manganese in seawaters globally, which range from 0.004 µg/L to 0.38 µg/L (Appendix A).

4.4 Reliability classification

The marine manganese DGVs have a moderate reliability classification (Warne et al. 2018) based on the outcomes for the following 3 criteria:

- sample size – 18 (preferred)
- type of toxicity data – combined chronic and acute (converted to chronic) data
- SSD model fit – good (inverse Weibull model).

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 (ACR)	The species' mean acute value (LC/EC50) divided by the chronic value (NOEC) for the same species.
Assessment factor	A unitless number applied to the lowest toxicity figure for a chemical to derive a concentration that should not cause adverse environmental effects. The size of the assessment factor varies with the type of data. Also called 'application factor' or 'safety factor'.
Benthic	Refers to organisms living in or on the sediments of aquatic habitats (e.g. lakes, rivers, ponds).
Chronic toxicity	A lethal or adverse sub-lethal 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. site-specific value), in the *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*. Formerly known as 'trigger value'.
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, 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.
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 organisms as compared to the controls. The statistical significance is measured at the 95% confidence level.
PC_x	Protective concentration for x% of species, where x = 80, 90, 95 or 99.
ROS	Reactive oxygen species.

Term	Definition
Site-specific	Relating to something that is confined to, or valid for, a particular place. Site-specific guideline values are relevant to the location or conditions that are the focus of a given assessment.
Species sensitivity distribution (SSD)	A method that plots the cumulative frequency of species sensitivity 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: dissolved manganese concentrations in marine waters

Table A1 Concentrations of dissolved (< 0.2-µm or < 0.45-µm filtered) manganese in marine waters with different levels of anthropogenic influence

Location	Dissolved Mn (µg/L)	Reference
Minimal anthropogenic influence		
Open ocean		
Global seawater, GEOTRACES	0.004–0.27	Bruland et al. (2014)
North Pacific Ocean	0.0055–0.055	Bruland et al. (1994)
North-west and south-west Atlantic Ocean	0.005–0.11	Van Hulten et al. (2017)
Southern Ocean from Tasmania to Antarctica	0.010–0.036	Latour et al. (2021)
Drake Passage, South America	0.01–0.12	Middag et al. (2012)
South-eastern Atlantic and Southern oceans	0.011–0.055	Boye et al. (2012)
Outside barrier reef, New Caledonia	0.05	Moreton et al. (2009)
Southern east Atlantic Ocean	0.055–0.16	Pohl et al. (2011)
North Atlantic Ocean	0.082–0.11	Hatta et al. (2015)
Coastal		
North coast, Papua New Guinea	0.082–0.14	Mackey et al. (2002)
Reserve Merlet, New Caledonia	0.09–0.11	Moreton et al. (2009)
Gulf of California, Mexico	0.11–0.38	Delgadillo-Hinojosa et al. (2006)
Middle lagoon, New Caledonia	0.13	Moreton et al. (2009)
Moderate anthropogenic influence		
Black Sea, Eurasia	0.03–40	Zeri et al. (2000)
Canal de la Havannah, New Caledonia	0.13–0.24	Moreton et al. (2009)
North Aegean Sea, Eurasia	0.19–2.5	Zeri et al. (2000)
The Narrows and Port Curtis, Australia	< 0.2–7	Angel et al. (2010)
Bay de Prony, New Caledonia	0.25–0.43	Moreton et al. (2009)
Boulari Bay, New Caledonia	0.29–0.83	Moreton et al. (2009)
Dumbea Bay, New Caledonia	0.32–2.3	Moreton et al. (2009)
Port Jackson, Australia	0.32–100	Hatje et al. (2003) and Jahan and Strezov (2017)
Taiwan Strait, Taiwan	0.46–1.3	Fang et al. (2006)
Baie de St Vincent, New Caledonia	0.94–2.5	Moreton et al. (2009)
Port Kembla, Australia	1–9	Jahan and Strezov (2017)
Port Eden, Australia	1–51	Jahan and Strezov (2017)
Port Newcastle, Australia	1–34	Jahan and Strezov (2017)
Anse Vata, New Caledonia	1.32	Moreton et al. (2009)
Grande Rade, New Caledonia	1.4–2.0	Moreton et al. (2009)
Port Moselle, New Caledonia	2.5	Moreton et al. (2009)

Location	Dissolved Mn (µg/L)	Reference
Port Botany, Australia	2–6	Jahan and Strezov (2017)
Port Yamba, Australia	9–44	Jahan and Strezov (2017)
Rio Doce estuary, Brazil	582	Queiroz et al. (2021)
Anoxic waters		
East China Sea	0.082–7.7	Wang et al. (2016)
Black Sea, Eurasia	440	Yemenicioglu et al. (2006)
Baltic Sea, Europe	55–260	Yakushev et al. (2009)
Hydrothermal		
Northeast Lau Basin, Pacific Ocean	3–103	Baumberger et al. (2020)
Gakkel Ridge, Arctic Ocean	0.27	Middag et al. (2011)
Mid-Atlantic Ridge	3.9	González-Santana et al. (2020)
Marine sediment porewaters		
Bay de Prony sediment porewater, New Caledonia	443–1,964	Moreton et al. (2009)
Northern Gulf of Mexico sediment porewater, USA	11,000	Lenstra et al. (2022)

Appendix B: toxicity data for coral species

Table B1 Manganese toxicity data for coral species and isolated symbiont dinoflagellates

Species	Life stage	Exposure duration (hours)	Test type	Biological endpoint	NOEC (µg/L)	LOEC (µg/L)	EC10 (µg/L)	EC20 (µg/L)	EC50 (µg/L)	Reference
Acropora millepora	Adult	336	Chronic	Tissue sloughing	> 1,090	—	—	—	—	Golding et al. (2023)
	Adult	48	Acute	Tissue sloughing	906	2,410	1,300 (910–1,690)	1,590 (1,220–1,970)	2,560 (2,220–2,900)	Golding et al. (2023)
Acropora muricata	Adult	48	Acute	Tissue sloughing	—	—	227 (19–436)	—	728 (399–1,100)	Binet et al. (2023)
	Adult	48	Acute	Tissue sloughing	—	—	281 (57–505)	—	933 (662–1,200)	Binet et al. (2023)
Acropora spathulata	Adult	48	Acute	Tissue sloughing	—	—	50[a]	—	700[a]	Summer et al. (2019)
	Adult	48	Acute	Mortality	—	—	1,800[a]	—	2,700[a]	Summer et al. (2019)
	Larva	72	Acute	Mortality	—	17,000	—	—	7,000[b]	Summer et al. (2019)
	Larva	24	Acute	Mortality	17,000	36,000	4,000[b] (0–9,000)	—	28,000 (24,000–23,000)	Summer et al. (2019)
	Gamete	5.5	Chronic	Fertilisation[c]	72,000	108,000	15,000 (0–38,000)	—	237,000 (199,000–304,000)	Summer et al. (2019)
Platygyra daedalea	Gamete	5.5	Chronic	Fertilisation[c]	54,000	71,000	43,000 (33,000–58,000)	—	164,000 (125,000–249,000)	Summer et al. (2019)
Stylophora pistillata	Adult	48	Acute	Tissue sloughing	510	—	—	—	860 (700–1,000)	Stauber et al. (2002)
	Adult	48	Acute	Mortality	1,100	—	—	—	1,500	Stauber et al. (2002)
Dinoflagellates isolated from coral *S. pistillata*	—	48	Acute	Quantum yield	1,000	—	—	—	> 1,000	Stauber et al. (2002)
	—	48	Acute	Dinoflagellate density	1,000	—	—	—	> 1,000	Stauber et al. (2002)
Dinoflagellates isolated from coral *Heliofungia actiniformis*	—	6	Acute	Quantum yield	> 200,000	—	—	—	—	Stauber et al. (2002)

[a] Toxicity value is based on nominal manganese (all other toxicity values are based on measured dissolved [< 0.45-µm filtered] manganese) and was part of a pilot test with low replication.
[b] Toxicity estimate is extrapolated below the lowest test concentration.
[c] Results for fertilisation could not be replicated, and the use of the NOEC/LOEC was suggested as being more appropriate than the EC10 or EC50 (Summer et al. 2019). 95% confidence limits are shown in parentheses where available.

Appendix C: toxicity data that passed the screening and quality assessment and were used to derive the default guideline values

Table C1 Summary of the toxicity data that passed the screening and quality assurance processes for manganese in marine water

Taxonomic group (phylum or clade)	Species	Life stage	Exposure duration (hours)	Test type	Toxicity measure (endpoint)[a]	Test medium	Temperature (°C)	Salinity (PSU)	pH	Toxicity value (µg Mn/L)[b]	Reference
Diatom	*Ceratoneis closterium*[c]	NR	72	Chronic	NOEC (growth rate)	Filtered seawater	NR	NR	NR	**18,000**	Levy et al. (2004)
Golden microalga	*Tisochrysis lutea*[d]	Log phase	72	Chronic	NOEC (growth rate)	Filtered seawater	25	34–35	8.0–8.2	**125,000**	ESA (2008)
Cnidarian (coral)	*Acropora millepora*	Adult	336	Chronic	NOEC (tissue sloughing)	Filtered seawater	27	35–36	8.1	**≥ 1,090**	Golding et al. (2023)
	Acropora muricata	Adult	48	Acute	EC50 (tissue sloughing)	Filtered seawater	27	36	8.1	317[e]	Binet et al. (2023)
		Adult	48	Acute	EC50 (tissue sloughing)	Filtered seawater	27	36	8.1	406[e]	Binet et al. (2023)
										358	**Geometric mean**
	Acropora spathulata	Adult	48	Acute	EC50 (tissue sloughing)	Unfiltered seawater	24	37	8.3	**304**[e,f]	Summer et al. (2019)
	Platygyra daedalea	Gametes	5.5	Chronic	NOEC (fertilisation)	Unfiltered seawater	24	37	8.3	**54,000**	Summer et al. (2019)
	Stylophora pistillata	Adult	48	Acute	EC50 (tissue sloughing)	Filtered seawater	23	NR	NR	**374**[e]	Stauber et al. (2002)
Echinoderm (sea urchin)	*Heliocidaris tuberculata*	Embryo	72	Chronic	NOEC (embryo development)	Filtered seawater	20	36	8	2,500	ESA (2008)
		Embryo	72	Chronic	NOEC (embryo development)	Filtered seawater	19	32	8	1,000	Levy et al. (2004)
										1,580	**Geometric mean**
Mollusc (bivalve)	*Anadara trapezi*	Embryo	48	Chronic	NEC (embryo development)	Filtered seawater	21	30	7.9	**1,040**	Markich (2021)
	Barnea australasiae	Embryo	48	Chronic	NEC (embryo development)	Filtered seawater	21	30	7.9	**1,780**	Markich (2021)

Taxonomic group (phylum or clade)	Species	Life stage	Exposure duration (hours)	Test type	Toxicity measure (endpoint)[a]	Test medium	Temperature (°C)	Salinity (PSU)	pH	Toxicity value (µg Mn/L)[b]	Reference
	Fulvia tenuicostata	Embryo	48	Chronic	NEC (embryo development)	Filtered seawater	21	30	7.9	**1,460**	Markich (2021)
	Hiatula alba	Embryo	48	Chronic	NEC (embryo development)	Filtered seawater	21	30	7.9	**1,520**	Markich (2021)
	Irus crenatus	Embryo	48	Chronic	NEC (embryo development)	Filtered seawater	21	30	7.9	**2,410**	Markich (2021)
	Magallana gigas[g]	Embryo	48	Chronic	NEC (embryo development)	Filtered seawater	21	30	7.9	**650**	Markich (2021)
	Saccostrea glomerata[h]	Embryo	48	Chronic	NEC (embryo development)	Filtered seawater	21	30	7.9	**654**	Markich (2021)
	Scaeochlamys livida	Embryo	48	Chronic	NEC (embryo development)	Filtered seawater	21	30	7.9	**959**	Markich (2021)
	Spisula trigonella	Embryo	48	Chronic	NEC (embryo development)	Filtered seawater	21	30	7.9	**2,090**	Markich (2021)
	Xenostrobus securis	Embryo	48	Chronic	NEC (embryo development)	Filtered seawater	21	30	7.9	**755**	Markich (2021)

[a] The measure of toxicity being estimated/determined: NEC: no-effect concentration; NOEC: no-observed-effect concentration; EC50: median-effect concentration.
[b] Bold values are the final toxicity values used in deriving the default guideline values.
[c] Formerly known as *Nitzschia closterium.*
[d] Formerly known as *Isochrysis galbana*.
[e] Estimated chronic toxicity value derived by dividing the acute EC50 by a coral-specific acute-to-chronic ratio of 2.3.
[f] Nominal concentration.
[g] Formerly known as *Crassostrea gigas*.
[h] Formerly known as *Saccostrea commercialis.*
NR = not recorded.

Appendix D: the influence of bivalve data on the species sensitivity distributions and default guideline values

The 10 bivalve mollusc species from Markich (2021) comprised 56% of the final dataset (i.e. 10 of the 18 toxicity values). Apart from the Markich (2021) data, there were no other data for bivalves of sufficient quality available for the derivation. The influence of the large number of bivalve data from Markich (2021) on the SSD and associated protective concentration (PC) values was investigated by removing them from the dataset and examining the changes in the SSD fit (Figure D1), PC values (Table D1) and PC value reliability. The inclusion of the Markich (2021) bivalve data improved the fit of the SSD and increased the PC values by a factor of 1.2–2.4 compared to the dataset without the bivalve data. Notwithstanding the additional data and improved fit of the SSD when the bivalve data were included, the reliability of the PC values did not change (i.e. remained as moderate reliability) due to the inclusion of the acute (converted to chronic) data for the adult corals in both datasets. Based on the assessment, the Markich (2021) bivalve data were included in the final dataset due to the increased number of data (n = 18 instead of n = 8) and taxonomic representation (n = 5 instead of n = 4) that they provided for the dataset and the improved fit of the SSD.

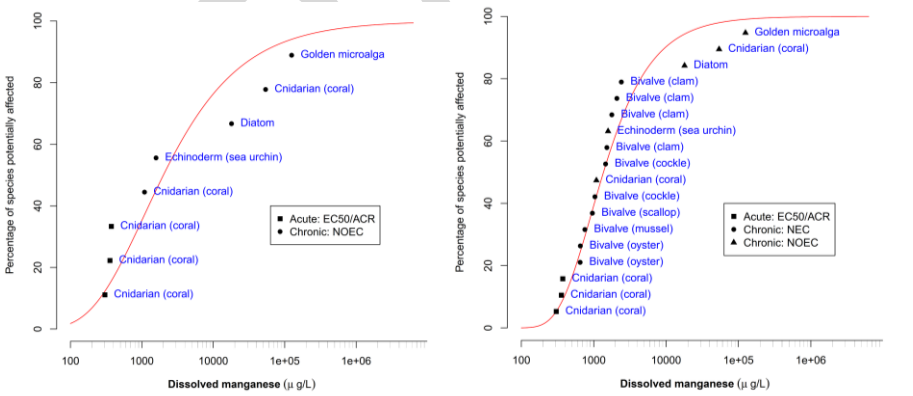

Figure D1 Species sensitivity distributions for dissolved manganese in marine water without the Markich (2021) bivalve data (n = 8) (left) and with the Markich (2021) bivalve data (n = 18) (right)

Table D1 Protective concentration values for dissolved manganese in marine water with and without the Markich (2021) bivalve data

	Protective concentration (PC) values for dissolved manganese in marine water (µg/L)[a]	
Level of species protection (%)	**Without Markich (2021) data (n = 8)**	**With Markich (2021) data (n = 18)**
99	80	190
95	170	300
90	260	390
80	480	570

[a] The PC values were derived using the Burrlioz 2.0 software and have been rounded to 2 significant figures.

Appendix E: modality assessment for manganese

A modality assessment was undertaken for manganese according to the 4 questions stipulated in Warne et al. (2018). These questions and their answers are listed below. It is important to note that the small sample size of the dataset makes it difficult to draw conclusions about modality.

1. Is there a specific mode of action that could result in taxa-specific sensitivity?

Manganese is an essential element for all life and there is no known mode of toxic action that would be specific to a taxonomic group.

2. Does the dataset 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.

The histograms of the raw data and log-transformed data (Figure E1) are not normal and have a positively right-skewed tail. This is due to 15 of the 18 toxicity values being between 304 µg/L and 2,410 µg/L and 3 toxicity values being ≥ 18,000 µg/L.

When the BC is > 0.555, it indicates that the data do not follow a normal distribution and may be bimodal. The BC of the log-transformed data is 0.889, which supports an assertion of bimodality. However, it is likely that this is a right-skewed unimodal dataset that has produced an erroneously high BC value, as discussed further by Pfister et al. (2013).

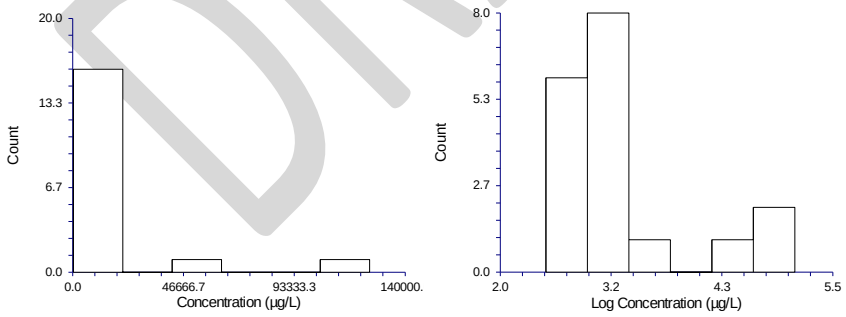

Figure E1 Histograms showing untransformed (left) and log-transformed (right) data

3. Do data show taxa-specific sensitivity (i.e. through distinct groupings of different taxa types)?

The box plots (Figure E2) suggest that the sensitivity of corals covers a broad range, due to the higher sensitivity to manganese of adult corals compared to early life stages (Binet et al. 2023). Bivalves have a much narrower range of sensitivity, which overlaps with that of corals and sea urchins, while microalgae seem more tolerant. No one taxonomic group appears more sensitive than all others to manganese, although the sample sizes are too small to make definitive conclusions.

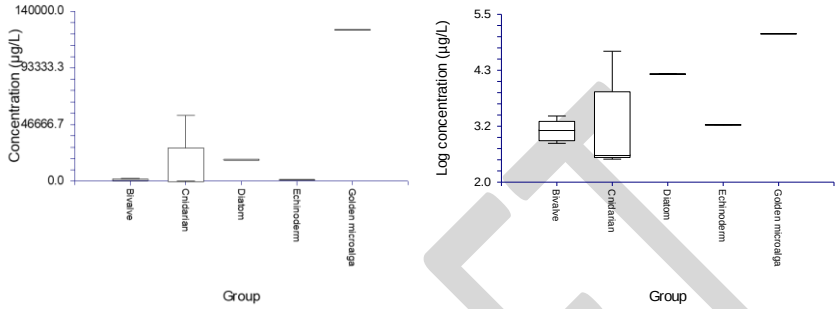

Figure E2 Box plots showing untransformed (left) and log-transformed (right) data grouped by taxonomic group

4. 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?

The weight-of-evidence approach produced mixed results for bimodality. Although there was some evidence for bimodality (i.e. BC above the indicative bimodality threshold of 0.555), this result was probably a function of the dataset being positively right-skewed (see Pfister et al. 2013). The dataset is small (n = 18) and there is no distinct clustering of taxa. Manganese is not known to exhibit a specific mode of action that would target a specific taxonomic group and, accordingly, there was little evidence of taxa-specific sensitivity to manganese. Relatively high sensitivity to manganese among corals appears to be restricted to adults. Early life stages are less sensitive. The balance of evidence suggests that the dataset is unimodal with a positively right-skewed tail rather than bimodal (Figure E1).

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