8.2 Heavy metals in freshwater

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Citation for this chapter: Tremblay, L. (2024). Heavy metals in freshwater. *In:* Lohrer, D., et al. *Information Stocktakes of Fifty-Five Environmental Attributes across Air, Soil, Terrestrial, Freshwater, Estuaries and Coastal Waters Domains*. Prepared by NIWA, Manaaki Whenua Landare Research, Cawthron Institute, and Environet Limited for the Ministry for the Environment. NIWA report no. 2024216HN (project MFE24203, June 2024). [https://environment.govt.nz/publications/information-stocktakes-of-fifty-five-environmental-attributes]

Alternative attribute name: Trace metals in freshwater

State of Knowledge for the "Heavy Metals in freshwater" attribute: Good / established but incomplete – general agreement, but limited data/studies

Part A—Attribute and method

A1. How does the attribute relate to ecological integrity or human health?

Trace metals are naturally present in the environment. Their distribution depends on the presence of natural sources (e.g., volcanoes or erosion) and human activities through extraction from ores [1]. The main anthropogenic activities resulting in the discharge of metals include fossil fuel combustion, industrial and agricultural processes and many metals are used in daily home activities [2].

The term heavy metals is often used to describe metals in general. However, it is not appropriate as not all metals are heavy or non-essential. For instance, cadmium and mercury are heavy metals but other metals of environmental concern including zinc and copper are essential metals. It is estimated that one-third of all proteins requires a metal cofactor for normal functions [1]. However, even essential metals can be toxic and that depends on the concentration. This relates to the concept of essentiality as illustrated in Figure 1. For essential metals like copper, zinc and selenium, there is a "window of essentiality" which represents a range of concentrations that will maintain a level of health in an organism- as illustrated in Figure 1A. For non-essential metals like cadmium, when concentrations reach levels that overcome the defence capacity of an organism, then it becomes toxic (Figure 1, panel B). This is why using trace metals is the appropriate term to use as it covers all metals. The most appropriate term would be trace elements as arsenic is defined as an element or metalloid.

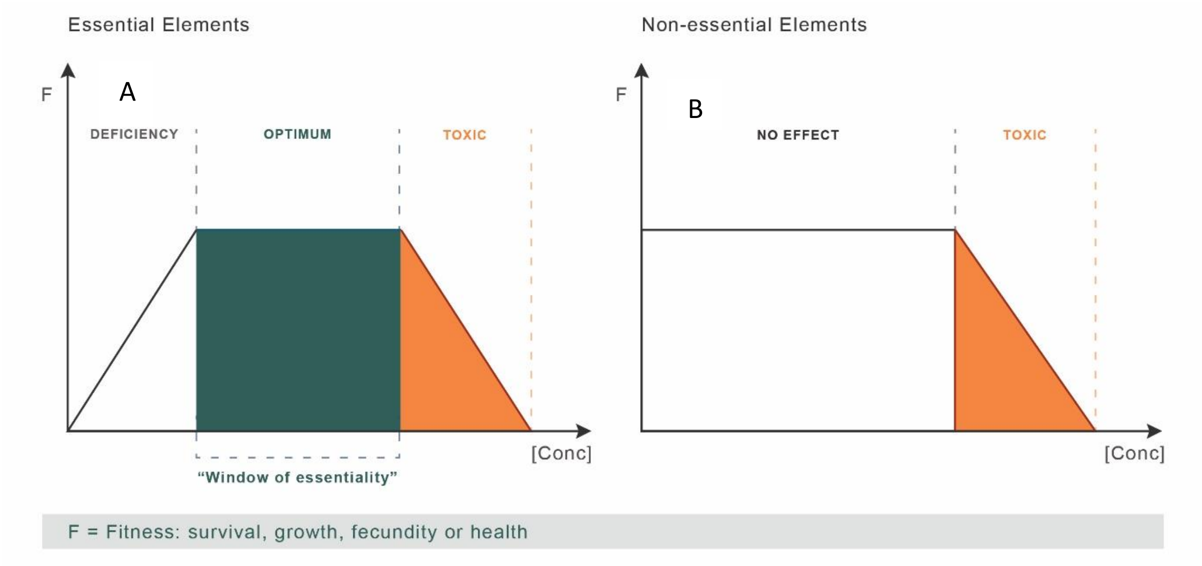

Figure 1. Conceptual diagrams illustrating the differences in concentration–response relationships with respect to organism health between A) essential metals and B) non-essential metals.

The toxicity of trace metals is well established and can impact both ecosystem and human health. Metals and metal compounds can interfere with functions of the central nervous system (CNS), the haematopoietic system, liver and kidneys [2].

A2. What is the evidence of impact on (a) ecological integrity or (b) human health? What is the spatial extent and magnitude of degradation?

There is strong evidence globally of the adverse effects on human metabolism resulting from exposure to metal-contaminated drinking water [3]. Exposure to non-essential metals is potentially harmful as they do not have physiological roles in the metabolism of cells. In addition, the ingestion of metals via food or water can modify the metabolism of other essential elements including zinc, copper, iron and selenium [2]. The general mechanism of heavy metal toxicity is through the production of reactive oxygen species (ROS) leading to oxidative damage and subsequently, adverse effects on health [3]. The disruption of metal ion homeostasis leads to oxidative stress through the formation of ROS which overwhelm body antioxidant protection and subsequently induces DNA damage, lipid peroxidation, protein modification and other effects, all symptomatic of numerous diseases, including cancer, cardiovascular disease, diabetes, atherosclerosis, neurological disorders (Alzheimer's disease, Parkinson's disease), chronic inflammation and others [4]. Another important mechanism of toxicity is the bonding of redox inactive metals like cadmium, arsenic and lead to sulphydryl groups of proteins and depletion of glutathione [4]. The mechanisms of toxicity are conserved, and metals affect ecosystem health in a similar way.

Waterbodies in areas of high anthropogenic activity like urban centres and areas of intensive agriculture are more likely to be contaminated with metals. Urban areas have larger areas of impervious surfaces such as roofs, roads and paved areas that are sources of metals [5]. Stream water quality changes in urban and rural areas as development both increases the generation of contaminants and changes the transport and processing of contaminants. Many urban and rural streams are also the receiving environment for untreated sewage, via leakage or overflows from wastewater networks and treatment plants.

Increasing population pressure and urbanization of the coastal zones have resulted in a variety of chronic impacts operating on coastal and estuarine ecosystems. Land-based activities affect the runoff of pollutants and nutrients into fresh and coastal waters affecting biodiversity and ultimately the provision of ecosystem services . Local studies in the Auckland coastal zone and the Tauranga Harbour showed ecological health decline, based on community structure composition changes along a pollution gradient, occurring at metal levels below guideline threshold values . These are good examples that coastal ecosystems are often exposed to multiple stressors and robust management frameworks are required to consider the presence of multiple physical and chemical stressors. Similar considerations apply in the freshwater domain.

A3. What has been the pace and trajectory of change in this attribute, and what do we expect in the future 10 - 30 years under the status quo? Are impacts reversible or irreversible (within a generation)?

There are multiple sources of metals. Natural sources of metals include rocks, ore minerals, volcanoes, and weathering releases of metals during soil formation transported to the surface and/or aquifer waters. The primary anthropogenic sources of metals are related mostly to the mining, extraction, and refining stages of ore that can lead to air, water, and soil pollution [11]. Metals are elements that can neither be created nor destroyed so once they are extracted from ore, they may be dispersed into the environment where they can accumulate [1]. Metals are transported from secondary sources into waterways via stormwater from roads (zinc from tyre wear, copper from brake pad wear); roofs (zinc from galvanised roofing); and other impervious surfaces (including paved areas around industrial sites) [12].

Copper and zinc are major contaminants in urban streams and frequently used as indicators of stormwater inputs [5]. For state of the environment reporting, the accumulation of metals has been monitored over the years, primarily in the main centres of Auckland, Wellington and Christchurch. The data is publicly available. For instance, between January 2015 and December 2017 median concentrations of dissolved zinc exceeded the Australian and New Zealand Guidelines for Freshwater and Marine Water Quality default guideline values (DGVs) at 8 of 11 Auckland sites, 3 of 5 Wellington sites, and 13 of 39 Christchurch sites[1]. The trends for dissolved zinc and copper at sites monitored between 2011 and 2017 varies from improving to worsening. The analysis of a range of parameters including dissolved zinc indicates that if urban development continues its' current trend, increases in urban land cover around New Zealand can be expected to result in further declines in water quality and a reduced likelihood that water quality objectives will be achieved at impacted locations [5].

For metal physiology and toxicology, the importance of chemical speciation cannot be overstated. Perhaps the simplest feature of speciation is whether the metal is in the dissolved or particulate form. This reflects the general recognition that particulate metals exhibit negligible toxicity and bioavailability to aquatic organisms relative to dissolved metals. The speciation chemistry of different metals varies greatly, but in general lower pH increases the free ion concentration, thereby increasing toxicity, whereas alkalinity (i.e., bicarbonate - HCO_3) and inorganic anions tend to complex metal ions, thereby decreasing toxicity. The hardness cations (Ca^{2+} and Mg^{2+}) as well as Na^+ and K^+ (and sometimes H^+) may also decrease toxicity by competing for metal binding sites on the gills of fish. The presence of dissolved organic matter (DOM) in most water bodies is another effective agent of protection against most metals [1]. Therefore, as metals continue to accumulate and partition into

[1] https://www.stats.govt.nz/indicators/river-water-quality-heavy-metals

the receiving environments, the bioavailability and ultimately the risk of these metals are highly dependent on the speciation conditions specific to that environment.

A4-(i) What monitoring is currently done and how is it reported? (e.g., is there a standard, and how consistently is it used, who is monitoring for what purpose)? Is there a consensus on the most appropriate measurement method?

Some metals are monitored as part of the State of Environment (SoE) reporting. Councils are conducting routine analyses for the occurrence and trends of metals for coasts, rivers, lakes and groundwaters as part of SoE monitoring and to meet consent condition requirements [13]. The SoE monitoring by regional councils focuses on a set of metals as reported in the recent Parliamentary Commissioner for the Environment (PCE) report on regulating the environmental fate of chemicals [1]. Monitoring of metal residues in relation to determining compliance with consent conditions is also often conducted for landfill leachate, wastewater and stormwater discharges [13].

The Australian and New Zealand Guidelines for Fresh and Marine Water Quality (https://www.waterquality.gov.au/anz-guidelines) are key tools to help planners, regulators and researchers to manage the quality of our water in New Zealand, especially for metals which are not currently covered by the NPS-FM. They provide default guideline values (DGVs) for all metals. These DGVs have been jointly developed by the Australian and New Zealand governments.

There have been notable advances in the development of bioavailability models for assessing toxicity as a function of water chemistry in freshwater ecosystems. For instance, the biotic ligand model (BLM), the multiple linear regression model, and multimetal BLM have been developed for most of the common mono- and divalent metals. Species sensitivity distributions for many metals are available, making it possible for many jurisdictions to develop or update water quality criteria or guidelines [15].

A4-(i) What monitoring is currently done and how is it reported? (e.g., is there a standard, and how consistently is it used, who is monitoring for what purpose)? Is there a consensus on the most appropriate measurement method?

The author is not in a position to comment, but Regional Councils have selected sites where they monitor trends for SoE reporting. Consent holders would also have access to sites for monitoring as part of their consent conditions.

A4-(iii) What are the costs associated with monitoring the attribute? This includes up-front costs to set up for monitoring (e.g., purchase of equipment) and on-going operational costs (e.g., analysis of samples).

The analytical methods using inductively coupled plasma mass spectrometry (ICP-MS) instruments can measure elements and metals and are well established and validated. Several commercial laboratories including Hill Labs and AsureQuality can measure metals at competitive prices.

A Jacobs investigation reported limitations that councils have identified that prevent the expansion of current monitoring programmes including the high costs for both laboratory analysis and council staff time spent doing monitoring and reporting [13].

[1] https://pce.parliament.nz/publications/regulating-the-environmental-fate-of-chemicals/

A5. Are there examples of this being monitored by Iwi/Māori? If so, by who and how?

We are not aware of any monitoring of this attribute being regularly undertaken by iwi/hapū/rūnanga. Resourcing is difficult for iwi/hapū/rūnanga to obtain, and any monitoring by agencies is generally infrequent, inconsistent, and ad hoc, and most programmes fail to provide information on whether chemical contaminants will have impacts of concern to Māori [28]. The Waikato River Report Card and other environmental assessment frameworks being developed by/with iwi/hapū/rūnanga include "safe to eat" or "safe to swim" outcomes [29-31]. Data/indicators required to fully realise these holistic cultural assessment frameworks will require information about heavy metals in water, sediment, and/or mahinga kai species.

A6. Are there known correlations or relationships between this attribute and other attribute(s), and what are the nature of these relationships?

Metals are often not the only type of contaminants at impacted sites. The issue of multiple stressors – e.g., stormwater and wastewater contain a range of other contaminants. Therefore, management of fresh and coastal waters must contend with multiple drivers in concert as the coordination of regulating agencies for urban and agricultural runoff is warranted [8]. As such, metals are only one component within a range of other contaminants that can accumulate in the environment.

Metals can be assimilated by, and bioaccumulate within organisms. Riparian vegetation would be expected to assimilate metals from surface and subsurface water passing through their root zones and from contaminated sediments deposited in riparian areas (see Riparian margin establishment and protection attribute).

Part B—Current state and allocation options

B1. What is the current state of the attribute?

The ecotoxicological effects of metals and their speciation under a range of environmental conditions are well understood and documented (as per references cited above). The key anthropogenic sources are well characterised to assist the management of these contaminants. The main challenge is that the management of metals requires a holistic/system approach as there are multiple factors to consider. For instance, roof material often contains zinc that can leach overtime. Some effort is required to find alternative types of material with less impacts. This needs to be underpinned by appropriate policy and evidence shows that this can be effective. For instance, the global phase-out of leaded petrol use has contributed to the decline of concentrations in the ocean [18].

B2. Are there known natural reference states described for New Zealand that could inform management or allocation options?

Finding reference sites with low levels of anthropogenic pressure could provide a baseline to confirm adverse impacts of metals and other stressors on receiving ecosystems. However, it is very difficult to find reference sites that experience no anthropogenic pressure.

The hazards of metals and their mechanisms of toxicity have been extensively characterised using model test species under controlled laboratory conditions. The data generated are used to derive the default guideline values (DGVs) which provide threshold values over which adverse impacts are expected. A metal concentration above a DGV should trigger further investigations to fully assess the impacts of the metal on the receiving ecosystem. Good baseline values can complement this approach by providing numeric evidence of concentrations expected in a healthy, unmodified ecosystem looks like is important. There are options to compensate for the lack of proper reference sites by monitoring across a gradient of stressors.

B3. Are there any existing numeric or narrative bands described for this attribute? Are there any levels used in other jurisdictions that could inform bands? (e.g., US EPA, Biodiversity Convention, ANZECC, Regional Council set limit)

There are well established default guideline values (DGVs) for a number of metals that have recently been reviewed by the Australian and New Zealand Guidelines for Fresh and Marine Water Quality [1]. These threshold values cover a range of protection levels of 80, 90, 95 and 99 % relevant to the particular ecosystem of interest, e.g., from industrial areas to national park and reserve areas.

B4. Are there any known thresholds or tipping points that relate to specific effects on ecological integrity or human health?

There are threshold value guidelines available. The ANZG DGVs have been developed to provide threshold values for metals and other contaminants. They are set to provide a range of protection as per point B3.

B5. Are there lag times and legacy effects? What are the nature of these and how do they impact state and trend assessment? Furthermore, are there any naturally occurring processes, including long-term cycles, that may influence the state and trend assessments?

As discussed in the above sections, metals have multiple anthropogenic sources and they can continue to accumulate in various environmental compartments including surface water, groundwater, and coastal waters due to the non-degradability of metals.

Natural background levels of metals in lakes and rivers may vary widely because of differences in local geology, and the aquatic organisms that live there tend to be genetically adapted to the local levels of metals. This adaptation is described as the “metalloregion concept” [8]. This is particularly relevant to New Zealand where levels of some metals in the environment are associated with our unique soil and volcanic activity. For instance, in the central North Island, arsenic is released from geothermal systems into the Waikato River [19]. The receiving ecosystems may have adapted to higher background levels, although in the case of the Waikato River system this has been extensively modified via the creation of hydrolakes for electricity generation which is likely to have altered the biota assemblages that now reside in those waterbodies.

B6. What tikanga Māori and mātauranga Māori could inform bands or allocation options? How? For example, by contributing to defining minimally disturbed conditions, or unacceptable degradation.

A high standard of water quality is an outcome sought by iwi/hapū/rūnanga. In addition to discussing this attribute directly with iwi/hapū/rūnanga, in regard to heavy metals in water, there is tikanga and mātauranga Māori relevant to informing bands, allocation options, minimally disturbed conditions

[1] www.waterquality.gov.au/anz-guidelines

and/or unacceptable degradation residing in treaty settlements, catchment/species restoration strategies, cultural impact assessments, environment court submissions, iwi environmental management plans, reports, etc.

For example, as result of the Waikato-Tainui Deed of Settlement, Te Ture Whaimana o te Awa o Waikato (the Vision & Strategy) is the primary direction setting document for the Waikato River and activities within its catchment affecting the river. In order to realise Te Ture Whaimana, 13 objectives and 12 strategies guide the restoration of the health and wellbeing of the Waikato River, including: "The restoration of water quality within the Waikato River so that it is safe for people to swim in and take food from over its entire length". The pilot Waikato River Report Card (Williamson et al. 2016), funded by the Waikato River Authority (WRA) and guided by a Waikato River Iwi Advisory Group, scored 'arsenic in water' between A-D using the ANZECC guidelines.

There are one-off-studies where iwi/hapū/rūnanga are influencing research initiatives exploring the state and impacts of environmental contaminants (including heavy metals) on the outcomes they are seeking (e.g., mauri is protected, kai is safe to eat, water is safe to swim) (e.g., [32-34]).

Part C—Management levers and context

C1. What is the relationship between the state of the environment and stresses on that state? Can this relationship be quantified?

The SoE reporting for MfE highlights the level of environmental degradation in both freshwater and marine domains [20, 21]. Metals are one of the multiple stressors that have been identified with sources including stormwater, municipal treated wastewater and agricultural discharges. There is evidence of interactive effects between copper and temperature on freshwater mussel species, suggesting the increased stress of elevated temperatures and copper exposure occurring together [22].

The toxicity and ecotoxicity of individual metals are well characterised and understood. However, predicting or assessing the environmental impacts of an individual chemical is a challenge in a field situation as contaminants are often found in complex mixtures. For instance, exposure to low levels of multiple chemicals in mixtures can cause toxicity at concentrations where exposure to an individual chemical might cause no effect based on their DGVs. This is because multiple physiological processes may be affected by chemicals having different mechanisms of toxicity. This is a strong argument for in favour of a systems approach to the management of aquatic systems.

C2. Are there interventions/mechanisms being used to affect this attribute? What evidence is there to show that they are/are not being implemented and being effective?

C2-(i). Local government driven

C2-(ii). Central government driven and C2-(v). Internationally driven

he Australian and New Zealand guidelines for Fresh & Marine Water Quality trigger values are designed to lead to further site-specific risk assessment. In a recent survey on the type and range of chemical contaminants that councils monitor, the emphasis was on the type of chemicals, but the implications of exceedance of DGVs was not assessed [13]. The author is not aware of any follow up studies in New Zealand in response to a DGV exceedance.

C2-(iii). Iwi/hapū driven

(iii) Treaty of Waitangi settlements have resulted in waterways/lakes/wetlands being returned to Māori ownership and/or management, many of which are in a highly degraded state. Many settlements include cultural redress packages to address the protection, restoration or rehabilitation of values, uses and services (and at scales) that have not previously been a strategic priority for research, restoration and monitoring by agencies. Treaty Settlements have also been the key drivers in the provision of new innovative approaches that bring together multiple knowledge systems together to inform co-management and restoration regarding values, species, catchments, and/or at scales that have not previously been prioritised by agencies.

Iwi/hapū/rūnanga are also influencing resource consent conditions which may include contaminant/bioaccumulation assessments that include heavy metals in water, sediments and/or mahinga kai species; however, generally these reports are not accessible in the public domain.

C2-(iv). NGO, community driven

Part D—Impact analysis

D1. What would be the environmental/human health impacts of not managing this attribute?

Metals are not degradable so any continuous discharges will accumulate metals into the various environmental compartments and biota. The impacts of human activities have pushed estuarine and coastal ecosystems far from their historical baseline of rich, diverse, and productive ecosystems [23]. The impacts on freshwater ecosystems from human activities have also been significant. Managing the sources of harmful contaminants is a priority to ensure the protection of these valuable ecosystems and to protect water supplies required for private and commercial uses from contamination. Encouragingly, there are examples of declining metal concentrations from improved environmental controls on emissions and discharges of metals and other contaminants, e.g., [24].

There are multiple challenges to reduce the discharge of metals in urban and rural environments, particularly non-point sources like stormwater. There are examples of options to reduce metals at-source summarised in the PCE report but these may be challenging to implement. For example, an initiative to impose restrictions on the maximum amount of zinc in galvanised or zinc coated roofing materials may be opposed by manufacturers of those materials [25].

D2. Where and on who would the economic impacts likely be felt? (e.g., Horticulture in Hawke's Bay, Electricity generation, Housing availability and supply in Auckland)

Fishery and aquaculture industries are most likely to be impacted by pressure from metal contamination. Healthy and functional ecosystems and healthy fish stocks are important for the fisheries industry [20]. There are other aspects to consider including natural beauty and recreational use of our freshwaters, estuaries, coastal and open ocean areas that are central to our culture and national identity. Furthermore, there are likely to be increased costs and economic impacts associated with the need for removal of trace metals from water supplies to ensure its safe use for drinking water, stock water, irrigation and other industrial and agricultural uses if this attribute were not managed.

D3. How will this attribute be affected by climate change? What will that require in terms of management response to mitigate this?

Climate change may alter physical, chemical and biological properties of ecosystems, affecting organisms but also the transport and fate of chemical pollutants. For example, an increase is storms is likely to mobilise contaminants in runoff in dissolved or particulate form. However, key concern with the effects of climate change on the risks associated with metal contamination is that changes to temperature and pH can modulate the speciation of metals or basically, their bioavailability. The importance of metal speciation cannot be overstated as it affects the bioavailability and toxicology of these materials. The simplest feature of speciation is whether the metal is in the dissolved or particulate form. Originally, environmental regulations were based on total metals present in the water as assayed by hot acid digestion of the samples. However, there has been a gradual change in many jurisdictions to regulations based on the dissolved component only. This reflects the general recognition that particulate metals exhibit negligible toxicity and bioavailability to aquatic organisms relative to dissolved metals [1]. Increases in temperature have been correlated with increasing toxicity of metals to aquatic organisms [26]. As such, temperature should be accounted for in risk assessment, because it may modify the effects of chemicals on the structure and functioning of aquatic communities, especially at higher levels of biological organization [27].

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