

Metals and Metalloids

Amanda Reichelt-Brushett and Graeme Batley

Contents

5.1	Introduction – 103
5.2	Sources of Trace Metals – 104
5.2.1	Natural Sources – 104
5.2.2	Anthropogenic Atmospheric Inputs – 105
5.2.3	Mining Operations – 106
5.2.4	Mineral Processing – 110
5.2.5	Urban and Industrial Discharges – 110
5.2.6	Other Sources – 111
5.3	Metal Behaviour in Marine Waters – 112
5.3.1	Metal Speciation – 112
5.3.2	Evaluating Metal Speciation and Bioavailability
	in Marine Waters – 114
5.4	Metal Behaviour in Marine Sediments – 114
5.4.1	Metal Forms in Sediments – 114
5.4.2	Metal Bioavailability in Sediments – 115
5.5	Metal Uptake by Marine Organisms – 116
5.5.1	Transport Across Biological Membranes – 117
5.5.2	Other Uptake Routes – 117
5.5.3	Metal Detoxification – 117
5.5.4	Metal Depuration – 117
5.6	Metal Toxicity to Marine Organisms – 118
F (1	Manager Tarifate to Mantes Distant 100

- 5.6.1 Mercury Toxicity to Marine Biota 120
- 5.6.2 Copper Toxicity to Marine Biota 120

© The Author(s) 2023

A. Reichelt-Brushett (ed.), *Marine Pollution—Monitoring, Management and Mitigation,* Springer Textbooks in Earth Sciences, Geography and Environment, https://doi.org/10.1007/978-3-031-10127-4_5

- 5.7 Managing Metal Pollution 121
- 5.7.1 What Is 'Pollution' 121
- 5.7.2 Guideline Values 121
- 5.8 Summary 121
- 5.9 Study Questions and Activities 122

References – 122

Acronyms and Abbreviations

AChE	Acetylcholinesterase activity
ASM	Artisanal and small-scale mining
ASGM	Artisanal and small-scale gold mining
ASS	Acid sulfate soils
AVS	Acid volatile sulfide
BLM	Biotic ligand model
CEC	Cation exchange capacity
DGT	Diffusive gradients in thin films
DGV	Default guideline value
DSTP	Deep-sea tailings placement
EC10	Concentration of a toxicant that causes a measured negative effect to 10% of a test population
GST	Glutathione S-transferase
ISA	International Seabed Authority
NOEC	No observed effect concentration
PNG	Papua New Guinea
POM	Particulate organic matter
TBT	Tributyltin
STD	Submarine tailings disposal (also known as DSTP)
USA	United States of America
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey

5.1 Introduction

This chapter introduces you to **metals** and **metalloids** that are a concern to the health of marine ecosystems. It provides a general chemical understanding of important metals and metalloids, their sources, behaviour, impacts and management. Metals, metalloids and non-metals all make up the periodic table (Appendix II) and are classified into these categories according to their properties. Metals are good conductors of heat and electricity and are malleable and ductile, making them very useful to humans and therefore economically valuable. Metalloids sit on the periodic table in a jagged line at the division between metals and non-metals and have intermediate properties.

You will come across various terms when studying metal pollution. **Trace metals** are generally referred to as those metals that are found in trace quantities in the environment although the term may also refer to those metals that are required in trace quantities in biological systems. The term **heavy metal** generally refers to density and excludes lighter metals (such as sodium and potassium) but is imprecise and has been questioned as useful (Chapman 2007, 2012; Batley 2012). Both terms are used to describe **metals of environmental concern** including aluminium (Al), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), molybdenum (Mo), silver (Ag), cadmium (Cd), gold (Au), mercury (Hg), tin (Sn) and lead (Pb). Metalloids of environmental concern include boron (B), arsenic (As) and antimony (Sb). Selenium (Se) is also sometimes referred to as a metalloid. As the electronics industry advances, rare earth elements are becoming more useful, and in the future, these elements may also be of environmental concern due to poor management of e-waste and other waste sources (e.g. Herrmann et al. 2016; Trapasso et al. 2021; Brewer et al. 2022). To assist with the flow of this chapter, metals and metalloids will generally be referred to as **metals** except when specific distinctions are necessary.

Most metals occur naturally in the environment, and at some places, they are found naturally in very high concentrations (e.g. in geological formations such as ancient volcanoes and deep ocean hydrothermal vents). They are found naturally in ocean waters (albeit at extremely low concentrations), sediments and rocks, and are transported to the ocean from terrestrial sources. The abundance and distribution of metals in the ocean are a function of their solubility in seawater and their degree of involvement in abiotic and biotic processes and oceanic circulation (Allen 1993). Some metals are essential to life and are required in small quantities, others have no known biological function (**•** Table 5.1).

Table 5.1 Essential and non-essential biotic requirements for metals of environmental concern			
Typical concentration	No known biological function in marine species	Probably essential (for some species)	Proven essential (for many species)
Trace (µg/g)			Fe, Zn, Cu
Ultra-trace (ng/g)	Au, Pb, Hg,	Ni, V, Sb, Cd ^b , As ^a	Mn, Co, Se, Mo, Cr
Adapted from Brady et al. (2015), other sources a Saunders et al. (2019), b Lane and Morel (2000)			

5.2 Sources of Trace Metals

Metals are naturally found in the marine environment, but through anthropogenic activities, they have increased in concentration in waters, sediments and biota. There are many thousands of research publications, from all areas of the world's rivers and oceans, that demonstrate the wide range of metal sources and their impacts on marine biota. An updated assessment of global emissions of metals to the environment (Table 5.2) has confirmed that anthropogenic sources far exceed natural sources with releases to soils being greater than those to water and the atmosphere (e.g. Salam, 2021).

5.2.1 Natural Sources

Most of the Earth's crust is composed of silicate minerals and rarer minerals that have been concentrated by one of the rock-forming processes (crystallisation,

metamorphosis and erosion and sedimentation). The formation of mineral deposits such as sulfide minerals of lead and zinc, and bauxite deposits of aluminium from the weathering of igneous rock, result in metal-enriched soils and sediments as they break down by natural weathering processes over geologic time. For this reason, natural background concentrations of metals in waters and sediments vary depending on the geological features in the related environments. For example, bauxite forms in rainy tropical climates and are associated with laterites and aluminous rock, depending upon climatic conditions in which chemical weathering and leaching are pronounced (Tarbuck and Lutgens 1987); deposits of nickel and cobalt are also found in laterites that develop from igneous rocks with high ferromanganese mineral contents (Tarbuck and Lutgens 1987). Maus et al. (2020) provided a timely update on mining activities at a global level which highlights where naturally rich mineral deposits exist. Globally, there are over 5650 mines associated with metals of en-

Table 5.2 Global emissions of metals to the environment					
Metal	Natural	Anthropogenic			Total
		Atmosphere	Water	Soil	
		10 ³ tonnes/y			
Mercury	2.5	2.0	4.6	8.3	14.9
Lead	12.0	119	138	796	1050
Arsenic	12.0	5.0	41.0	82.0	128
Cadmium	1.3	3.0	9.4	22.0	34.4
Zinc	45.8	57.0	226	1372	1655
Copper	28.0	25.9	112	955	1030
Selenium	9.3	4.6	41.0	41.0	86.6
Antimony	2.4	1.6	18.0	26.0	45.6
Tin	44.0	14.7	142	896	1940
Chromium	317	11.0	262	1670	194
Manganese	30.0	95.3	113	325	533
Nickel	26.0	240	12.0	132	384
Vanadium	3.0	2.6	11.0	88.6	102

5

• Table 5.3 Dissolved metal concentrations in ocean wa			entrations in ocean waters
	Metal	Coastal ocean water (ng/L)	References
	Aluminium	46	Rijkenberg et al. (2014) ^a
	Manganese	5	Angel et al. (2010)
	Iron	50	Rijkenberg et al. (2014) ^a
	Cobalt	3	Shelley et al. (2012) ^b
	Nickel	110	Angel et al. (2010)
	Copper	30	Apte et al. (1998)
	Zinc	22	Apte et al. (1998)
	Arsenic	1.5	Apte et al. (1998)
	Selenium	<73	Apte et al. (1998)
	Silver	<0.5	Apte et al. (1998)
	Cadmium	2	Apte et al. (1998), Angel et al. (2010)
	Mercury	<1	Apte et al. (1998)
	Lead	9	Apte et al. (1998)

^a Data for western Atlantic Ocean

^b Data for Sargasso Sea. All other data for NSW and Queensland coastal waters

vironmental concern in over 100 countries (Maus et al. 2020). The United States Geological Survey (USGS) provides an interesting interactive map of global mineral resources: https://mrdata.usgs.gov/general/map-global.html. In addition, there are rich mineral deposits of economic interest (but not yet mined) on the ocean floor (e.g. Heffernan 2019; Milinovic et al. 2021).

Metals from terrestrial sources can be transported to marine environments by dust, in catchment runoff and through the atmosphere. Volcanic eruptions contribute to the release of metals into the atmosphere and subsequent deposition into the marine environment (e.g. Gaffney and Marley 2014). In 1989, it was estimated that biogenic sources (natural sources) of metals contributed 30–50% of total metal emissions to the atmosphere (Nriagu 1989). As with most contaminants in the environment, the ocean is the ultimate sink for the vast majority of trace metals. Concentrations of met105

als of environmental concern in ocean waters are generally in the nanogram/litre range (Table 5.3) which are very difficult to quantify. The analytical process requires ultra-trace metal sampling and analysis procedures to ensure reliable estimations of baseline concentration against which to assess riverine and estuarine inputs.

5.2.2 Anthropogenic Atmospheric Inputs

Inputs of metals via the atmosphere from anthropogenic activities to the marine environment is an important pathway and, for mercury, it is the foremost transport pathway (Marx and McGowan 2011; Driscoll et al. 2013) (▶ Box 5.1). Interestingly, atmospheric lead was reportedly deposited in ice layers in Greenland between 500 BC and 300 AD and was expected to be a result of emissions from Roman mines and smelters (Nriagu 1989, 1996). Atmospheric distribution processes result in the deposition of metals throughout marine environments even where the human populations are very small (e.g. polar environments, Barrie et al. 1992; Rudnicka-Kępa and Zaborska 2021).

The **combustion of coal** liberates traces of Hg, Pb, Cr, Cd, Sn, Sb, Se, As, Mn and Ti, and exhaust emissions from the combustion of oil is a major source of nickel and vanadium (Pacyna and Pacyna 2001; Munawer 2018). The **combustion of leaded gasoline** was for many years determined to be the major source of atmospheric lead emissions (Pacyna and Pacyna 2001), although the phasing out of leaded fuels in most countries has seen these emissions decline. **Non-ferrous metal production** also contributes to atmospheric As, Cd, Cu, Sn and Zn (e.g. Pacyna and Pacyna 2001).

The largest atmospheric emissions of anthropogenic metals were estimated to come from Asia as a result of growing demands for energy in the region and increasing industrial production and limited regulatory controls (Pacyna and Pacyna 2001). Atmospheric deposition has been attributed to long-distance transport of Hg, Pb, Cd, As and Fe with enhanced loadings measured in polar regions and likely sources from Russia, China and Europe (Barrie et al. 1992; Driscoll et al. 2013; De Vera et al. 2021; Thorne et al. 2018).

Box 5.1: The Mercury Cycle

Mercury (Hg) is transported through the atmosphere from coal burning, oil refining, natural gas combustion, artisanal and small-scale gold mining, the chlor-alkali industry that produces chlorine and caustic soda, and waste incineration. Consumer goods such as batteries, electric switches, fluorescent lamps etc. all contain mercury) (Gaffney and Marley 2014) (\bullet Figure 5.1). Land and ocean processes play an important role in the redistribution of Hg through the environment, including to marine ecosystems. Toxic effects and biomagnification potential result from the net conversion of Hg(II) to monomethylmercury (CH₃Hg⁺) and dimethylmercury (CH₃)₂Hg). This conversion mostly occurs near the sediment:water



Figure 5.1 • Box 5.1: Current estimates of the fluxes (mg/y), pools and enrichment (%) of mercury at the Earth's surface. adapted from Driscoll et al. (2013) and citations therein by A. Reichelt-Brushett. This is an unofficial adaptation of an article that appeared in an ACS publication. ACS has not endorsed the content of this adaptation or the context of its use

interface and primarily in anoxic environments with sulfate-reducing bacteria (Scwartzendruber and Jaffe 2012). Such conditions are commonly found in wetlands, in river sediments, in the coastal zones and the upper ocean (Driscoll et al. 2013; Gerlach 1981). The production of methylmercury drives the major human exposure route via the consumption of fish, particularly higher order fish with the greatest potential for biomagnification (Driscoll et al. 2013). Initiatives such as the United Nations Global Mercury Partnership, set up in 2005, are helping global efforts to protect human health and the environment from mercury emission to the atmosphere, water and land (> https://www.unep.org/globalmercurypartnership/).

5.2.3 Mining Operations

Metal ore deposits are a vital resource for mineral processing facilities that recover purified metals for human use. The extraction and processing of ores enhances the mobilisation and distribution of metals throughout the environment. Mining operations on land areas adjacent or close to marine waters are potential sources of marine pollution. The **major contamination source arises from waste rock and mine tailings**. Depending on the local geology, these can be impounded in tailings dams, disposed of on nearby land in erodible dumps or transported to the ocean for **deep-sea tailings placement (DSTP)**.

Many ore deposits contain a combination of several metals and all of these can be contaminants at a single mining or processing site. In Thailand, for example, elevated concentrations of Pb, Zn, Cu and Fe were all found near tin mining and processing operations (Brown and Holley 1982). Other examples of mining, ore processing and/or tailings disposal that impinge on marine environments include copper in Chile, Indonesia and Papua New Guinea (PNG); manganese on Groote Island, Australia, and North Maluku Province, Indonesia; gold on Lihir Island, PNG, and Buyat Bay, Indonesia; aluminium in Gladstone, Australia; nickel in New Caledonia and PNG. Yanchinski (1981) noted that there were 56 large-scale mining operations in the Caribbean region alone. Ultimately, the marine environment is a major sink for terrestrial runoff and river and ocean discharges from mining activities.

Adequate waste management in mining operations is important for the protection of surrounding ecosystems and, in tropical regions, the restrictions on mining waste disposal are often related to the seasonal variations in rainfall (e.g. Holdway 1992). In many cases, there are agreed acceptable levels of discharge of overburden into the environment. The mining of copper and gold at Ok Tedi in PNG is an example of the difficulties associated with managing mine waste. Gold and copper mining on the Ok Tedi River (a tributary of the Fly River) was estimated to contribute 750,000 tonnes per day of copper-rich mine tailings and 90,000 tonnes of sediment per day to the river (Apte and Day 1998). High sediment loads containing significant concentrations of copper could be detected some 600 km downstream and beyond the mouth of the Fly River into the ocean (Apte et al. 1995). Elevated concentrations of

certain metals reported in seafood commonly eaten by Torres Strait Islanders prompted ongoing monitoring of Torres Strait metal concentrations (e.g. Gladstone 1996). Further study showed Ni, Cr, and As were elevated in sediments from the Gulf of Papua but less so in the Torres Strait (Haynes and Kwan 2002).

Significant unintentional impacts from landslides and erosion have occurred in mining operations in mountainous terrain with high rainfall (\triangleright Box 5.2). Such accidents highlight a need to develop sustainable approaches to mine tailings management and a range of alternatives such as tailings thickening and paste or cement production may be viable for some types of tailings (e.g. Adianyah et al. 2015; Saedi et al. 2021). Furthermore, such innovative technologies have the potential to address environmental problems for both the cement industry and tailings management (Saedi et al. 2021).

Box 5.2: Mariana Dam Disaster (Samarco Mine Tailing Disaster), Brazil

Dr. Pelli Howe, Environmental Scientist.

The collapse of an iron ore tailings dam in Mariana, Brazil, on the 5th of November 2015, has been described as Brazil's worst environmental disaster. Nineteen people were killed and the village of Bento Rodrigues was destroyed. 60 million m³ of iron-rich waste was released and contaminated 620 km of freshwater ecosystems before arriving at the Atlantic Ocean (via the Doce River mouth) 17 days after the collapse. The United Nations reported the immediate death of 11 million tonnes of fish, and that the flow of mud had destroyed 1469 ha of riparian forest. The plume spread over 2580 km² in surface waters, two times the natural plume observed two months before the incident and high concentrations of dissolved metals (Pb, Mn, and Se) were also detected in the plume (Frainer et al. 2016) and further studies indicate future metal bioavailability and contamination risk in estuarine soils (Queiroz et al. 2018).

The Doce River mouth is recognised in the Ramsar Convention (2016) due to its extremely high biodiversity. Serious concerns were raised for local populations of thousands of marine flora and fauna, including the two most endangered cetaceans of the Southwestern Atlantic Ocean: the Guiana dolphin (*Sotalia guianensis*) and the Franciscana dolphin (*Pontoporia blainvillei*) (Frainer et al. 2016; Miranda and Marques 2016).

Manslaughter charges were laid due to the evidence of negligence. However, on the 25th January 2019, another tailings dam in Brazil, Brumadinho Dam, owned by the same company, collapsed, releasing 11 million tonnes of tailings and killing an estimated 270 people (Cionek et al. 2019) (Figure 5.2).



■ Figure 5.2 ► Box 5.2: Tailings smother the land Mariana, Brazil. *Photo*: Senado Federal—Bento Rodrigues, Mariana, Minas Gerais, CC BY 2.0

Deep-Sea Tailings Placement

Continental margins or slopes are the boundary zones between the shallow shelf regions that surround most continents and the deeper abyssal plains of the sea floor. These areas have a steep profile, deep canyons and rugged topography (Ramirez-Llodra et al. 2010), which are the very features that make them attractive for DSTP, also known as submarine tailings disposal (STD). At the site of disposal (the end of a pipeline), which is usually between 50 and 150 m in depth, tailings spread over benthic communities (in the impact zone) (• Figure 5.3). The pipeline is preferably near a submarine canyon, and once discharged, tailings are expected to travel downslope to the deep-sea floor and settle. Tailings density, local upwelling, currents and other conditions will influence the likelihood of tailings redistribution and settlement (Reichelt-Brushett 2012).

DSTP operations currently occur in Chile, France, Turkey, Indonesia, PNG and Norway. Most are unconfined discharges into the deep ocean, but many, such as in Norway, use confined disposal into deep fjords at 30–300 m depth. In the coral triangle, a hot spot of global marine biodiversity, 19 past, current and proposed DSTP sites exist (e.g. Reichelt-Brushett 2012).

The load of tailings to the ocean from a single STD operation is in the order of 10–100 s of thousands of tonnes a day, with the actual amount being site-spe-

cific. Once tailings are disposed of at continental margins and into deep-sea environments, the metal availability and toxicity to organisms will depend on the physicochemical conditions specific to the location.

There are various other scientific considerations that should be considered in the risk assessment of DSTP (see Vare et al. 2018; Stauber et al. 2022). For example, the continental margins in general are characterised by many species-rich deep-sea communities, mostly dependent on food produced in the upper layers of the ocean (Glover and Earle 2004; Ramirez-Llodra et al. 2010). Coral and sponge communities flourish in these areas where currents carry food to them. The heads of canyons are often productive nursery areas for fish (Yoklavich et al. 2000; Howard et al. 2020). Most publications on deep-sea biodiversity highlight a limited understanding and the need for further studies. (e.g. Etter et al. 1999; Brandt et al. 2007; Baker et al. 2010; German et al. 2011; Ramirez-Llodra 2020). Furthermore, canyon topography influences current patterns and local upwelling, pumping nutrients into the euphotic zone which stimulates primary productivity (Fernandez-Arcaya et al. 2016 and references therein). Events such as large storm waves and underwater earthquakes along with dense water cascades and hyperpychal waters may trigger mass failures of unstable deposits in canyon heads and shelf edges (Fernandez-Arcaya et al. 2016 and references therein).



■ Figure 5.3 Conceptual diagram of submarine tailings disposal. *Image*: Reichelt-Brushett 2012, ■ Figure 5.3, CC BY 4.0: ► https://creativecommons.org/licenses/by/4.0

There is an important need to develop standardised risk assessment protocols that consider, environment, communities and cost-benefit analysis of alternatives. Precautionary principles should also be applied where knowledge is lacking, such as impacts of smothering, changes in water quality and contamination loads on ecosystem structure and function and diversity (many species are currently unknown to science).

Artisanal and Small-Scale Mining (ASM)

Between 10 and 15 million people in virtually all developing countries are involved in extracting over 30 different minerals using rudimentary techniques (Veiga and Baker 2004). Gold is the predominant metal extracted in **artisanal and small-scale mining** (ASM) (more specifically known as artisanal and small-scale gold mining (ASGM)) due to its high value and **easy extraction from ore using mercury** (• Figure 5.4). Koek-koek (2013) projected the annual amount of mercury released by ASGM in 70 countries to be 1608 tonnes. Such mining operations are often deemed illegal but provide pathways from poverty for rural communities.

This extraction process requires large volumes of water for flushing and results in the deposition of fine sediments and mercury in river systems and eventually the ocean, along with many other environmental and social problems (Velasquez-Lopez et al. 2010; Male et al 2013) (Figure 5.4b, c). Furthermore, the processing of the mercury–gold amalgam results in the volatilisa109

tion of mercury to the atmosphere. Unmapped legacy sites (\bullet Figure 5.4d), are commonly close to rivers and provide a source of mercury to the marine environment via catchment runoff. Mercury can then get into the food chain including commercial and small-scale fisheries (\triangleright Box 5.1). In some countries like Indonesia, with its many islands, large population and limited farmland, communities rely heavily on the ocean for protein resources and have high consumption rates, and in some communities, seafood is part of every meal (\bullet Figure 5.4e, f).

On Buru Island, Indonesia, gold was discovered in 2011 and ASGM commenced soon after. Sediment samples collected from the Wae Apu River and offshore from the river mouth just one year after the commencement of mining contained elevated mercury concentrations (Male et al. 2013). Several years later mercury concentrations in sediments had increased dramatically at some sites and some seafood sourced from the local fish markets also showed mercury concentrations of concern to human health (Reichelt-Brushett et al. 2017a).

Deep Seabed Mining

A new threat to marine ecosystems is the actual mining of the deep seabed. **Deep seabed mining** was raised as a possibility in the 1970s in the context of mining manganese nodules, but, at the time, technology and metal prices did not make the operations viable. Today, we



C Figure 5.4 Artisanal gold mining and food resources on Buru Island, Eastern Indonesia: **a** one of the mine sites (Gogrea) in operation; **b** trommel operations to crush ore and extract the with mercury. Water is used to flush the spent ore to the tailings ponds, **c** tailings ponds are designed with small trenches to overflow to the river, **d** abandoned trommel operations on the Wae Apu River bank, **e** up to 90% of protein comes from the marine environment in many areas of Eastern Indonesia, Buru Island fish markets, **f** wild harvest of mangrove molluscs. *Photos*: A. Reichelt-Brushett

have reached a point where such initiatives are economically viable and technological developments have aided in accessibility to the deep sea. Geologic exploration of the deep sea has identified many sites rich in a wide range of mineral resources. In PNG alone, there are 60– 100 exploration leases in deep waters around the island archipelagos. In 2018 one mine was in the verge of commercial operation in the sea near New Britain, PNG (Nautilus Minerals was developing the Solwara 1 copper and gold project, which is located at 1600 m depth). More recently, the mineral rich Clarion-Clipperton Zone in the Pacific, controlled by Nauru, has considerable commercial interest to extract cobalt and other metals.

As with DSTP operations, deep seabed mining is another risk to the health of marine ecosystems that we do not fully understand. The **deep sea represents the largest and the least explored environment on Earth** (e.g. Ramirez-Llodra et al. 2010). Along with the limited biological assessment mentioned earlier, less than 20% of the deep ocean floor has been mapped (seabed2030. org) and only a small fraction of it has been studied to assess its environmental, economic and social values. Studies are ongoing and new benthic and pelagic species and habitats are continuously being discovered.

Impacts of seabed mining may include the removal and compaction of the substrate and the generation of large sediment plumes, possibly containing toxic metals released from the sediments (Hauton et al. 2017; Washburn et al. 2019). The ecotoxicological effects on mid-water and benthic communities exposed to environmental changes such as these are generally not well understood (Drazen et al. 2020; Mestre et al. 2017; Washburn et al. 2019). Some information exists on the specialised biological communities and functioning of deep seabed ecosystems, but it is insufficient to properly assess the impacts of these pressures on them or on the services they may provide for the well-being of humans (van den Hove and Moreau 2007). There are knowledge gaps and transdisciplinary challenges associated with deep seabed mining which need to be addressed to ensure unexpected and unacceptable negative effects do not result (e.g. Reichelt-Brushett et al. 2022).

The International Seabed Authority (ISA) was established in 1994 (see also \blacktriangleright Chapter 16). It is comprised of 167 Member States, and the European Union is mandated under the UN Convention on the Law of the Sea to organise, regulate and control all mineral-related activities in the international seabed area for the benefit of mankind as a whole. In so doing, ISA has the duty to ensure the effective protection of the marine environment from harmful effects that may arise from deep seabed-related activities.

Drill Cuttings

The exploration and production of oil and gas reservoirs have resulted in large quantities of **drill cuttings** (drilling mud, speciality chemicals and fragments of reservoir rock) being deposited onto the seafloor. Elevated concentrations of Cr, Cu, Ni, Pb, Zn and Ba relative to the natural (background) concentrations in sediment have been measured in North Sea drill cutting accumulations (Breuer et al. 2004) and some drilling muds have been shown to be toxic to biota (Tsventnenko et al. 2000).

5.2.4 Mineral Processing

It is usual to transport ore concentrates from what are usually remote mine locations to more accessible mainland facilities where the ore is refined to produce pure metals. These facilities are typically located at coastal sites for shipping access and are a major source of trace metal contamination from ore spillage, site runoff and other discharges.

Largely due to the presence of one of the world's largest zinc smelters, the Derwent estuary was for many years the most polluted water body in Australia and arguably the world, resulting in some of the highest reported metal concentrations in sediments and shellfish (Macleod and Coughanowr 2019). Contaminants included Zn, Hg, Cd, Pb, Cu and As were contributed to also by discharges from Australia's largest paper mill.

Lake Macquarie in New South Wales, Australia, suffered extreme lead, zinc, cadmium and selenium contamination from the 100-year operation of a lead– zinc smelter in the north of the lake (Batley 1987), again with residual high concentrations in sediments affecting shellfish. The lead smelter at Port Pirie in South Australia (Lent et al. 1992) is a further example of historical impacts that remain a concern today. Internationally, there are many such examples of legacy contamination. Contamination sources are hopefully now being better managed, but the costs of remediating many years of sediment contamination are generally prohibitive.

5.2.5 Urban and Industrial Discharges

Urban harbours and waterways have long been the recipient of metal contaminants from a variety of sources including shipping, licensed industrial discharges, sewer overflows and sewage treatment plant discharges and stormwater. There are activities worldwide that are attempting to better manage these sources (Steinberg et al. 2016).

Elevated metal concentrations including (but not limited to) Zn, Ni, Pb, Hg, Cu and Cr in sediments and organisms have been related to discharges from **sewage outfalls** (e.g. Kress et al. 2004; Echavarri-Erasun et al. 2007) and the less well-developed the sewage treatment facilities the more likely for adverse effects. In China alone, the amount of **industrial sewage** discharged into the aquatic environment was estimated to be 21.7 billion tonnes in 2008 (NBSC 2009 in Pan and Wang 2012). The Yangtze River, the Pearl River and the Minjiang River are the main rivers that carry metals into coastal areas, all of which contributed over 78% of the total discharge of metals in 2008 resulting in alarmingly high metal concentrations in sediment, water and biota at some coastal locations in China (Pan and Wang 2012).

Power Stations

Coal-fired power stations represent a significant industrial source of metal contaminants to estuarine waterways. The direct discharges of cooling waters frequently contribute copper and zinc from brass fittings, while arsenic and selenium as leachable components of coal ash are present in overflows or releases from ash dams (Schneider et al. 2014).

Stormwater

Stormwater is a significant contributor to metal contaminants. Increased urbanisation has meant that stormwater that would have been absorbed on land is now being directed via gutters and drains to the nearest waterways. Sediment traps and artificial wetlands offer partial solutions in selected areas, but within major urbanised catchments, stormwaters remain the major source of metal contaminants to sediments (e.g. Lau et al. 2009; Birch et al. 2015; Becouze-Lareure et al. 2019).

5.2.6 Other Sources

Shipping

Most large ships (cruise ships, cargo ships, container ships, tankers and ore carriers) are today equipped with exhaust gas scrubbers that discharge contaminants to the sea that might otherwise be emitted to the atmosphere. Washwater discharges from these scrubbers contain vanadium and nickel (derived from fuel oil combustion) together with copper and zinc as the major metal contaminants (Turner et al. 2017).

All ships use antifouling paints to prevent marine growth on their hulls. For a long time, tributyltin (TBT) was the major biocide used until its banning on small ships in the late 1990s with a slower decline in its use on bigger vessels. With a leaching rate near $5 \mu g/cm^2/day$, it is a significant source of dissolved copper to the marine environment from both small ships in marinas and large vessels (Turner et al. 2017) (see \blacktriangleright Chapter 7 for detail on metal biocides and \blacktriangleright Chapter 8 for additional detail on TBT). Today, most antifouling paints are copper-based usually together with an organic biocide.

To protect steel hulls of large ships from corrosion, it is usual to fit sacrificial anodes, typically made of zinc or aluminium. As the anode supplies electrons to the cathode, it gradually dissolves, with the result that the steel cathode becomes negatively charged and protected against corrosion (Netherlands National Water Board 2008). For zinc anodes, release rates are typically $50-80 \ \mu g/cm^2/day$. Zinc is a ubiquitous environmental contaminant, so it is difficult to estimate the contribution of this source to sediments in ports and harbours.

Dredging

Dredging is an activity that has the potential to release metals into the marine environment both from the dredging sites in ports and harbours (e.g. Reichelt and Jones 1994; Montero et al. 2013), and from the dredge spoil disposal that typically occurs in relatively deep (<100 m) offshore waters. Such activities are controlled by the London Dumping Convention (NAGD 2009) (see also \triangleright Chapter 16) and the dredged sediment is contained within an agreed spoil ground. Consideration of the metals and their concentrations must be done prior to dredging activity in ports and harbours and dredge spoil dumping. Dredging physically disturbs and redistributes sediments, mobilising associated metals.

Shipwrecks and Dumping Sites

Shipwrecks are another source of metals. For example, the Gulf of Gdańsk, Poland, was an important place in Baltic trade routes and military activity, and numerous **shipwrecks** have been identified on its sea bed. Data published by the National Maritime Museum and the Maritime Office in Gdynia describe 25 wrecks in the Gulf of Gdańsk (NMM 2018 in Zaborska et al. 2019). Scientists observed that oil derivatives and metals from the *SS Stuttgart* wreck located near the entrance to the Port of Gdynia have contaminated a large part of the nearby sea bed (Rogowska et al. 2010, 2015).

Many other solid metal wastes have been dumped into the ocean, for example, the famous wreck dive site called Million Dollar Point in Vanuatu was created when the USA army dumped bulldozers, jeeps, trucks, semi-trailers, fork lifts and tractors off the point when they failed to come to a deal with the local community to buy the equipment and it was deemed cheaper to dump in the ocean rather than transport it back to the USA.

Agricultural Runoff

There are several sources of metals in **agricultural runoff**. For example, copper-based fungicides such as copper oxychloride are used in the agricultural industry and these may contribute to the contaminants in agricultural runoff. In addition, phosphate fertilisers naturally contain elevated concentrations of cadmium (Roberts 2014), and the cadmium concentration is directly correlated with the amount of total phos-

phorus in the fertiliser (e.g. Roberts 2014; Rayment 2011). Based on a nutrient budget for the tropical Port Moresby catchment, Eyre (1995) suggested that agricultural practices have caused a 2-fivefold increase in the phosphorus flux. This provides a potential source of cadmium to marine waters from land runoff, particularly during the wet season. The regulation of cadmium in commercial fertilisers has helped reduce the quantities of it entering cropping systems (Rayment 2011). See \triangleright Chapter 7 for more detail on metal-based pesticides and biocides.

Acid Sulfate Soils (ASS)

Acid sulfate soils (ASS) are soils or sediments that contain highly acidic soil horizons or layers affected by the oxidation of iron sulfides (actual ASS), and/or soils or sediments containing iron sulfides or other sulphidic materials that have not been exposed to air and oxidised (potential ASS). The term acid sulfate soil generally refers to both actual and potential ASS. The acidic leachates and dynamic porewater chemistry influence metal cycling and behaviour (e.g. Gröger et al. 2011).

Acid sulfate soils are found in North America, South America, Asia, Africa, Oceania and Europe. They are expansive through the east coast of the USA, the east and west coasts of Mexico and Africa, the northern and eastern countries of South America, Vietnam, India, Bangladesh, China, Indonesia, PNG and much of Australia (Proske et al. 2014).

In eastern Australia, most ASS layers were deposited in the Holocene Epoch (10,000 years ago to the present) as a consequence of post-glacial sea level rise and the subsequent stillstand (a period of stable sea level), during which there was an infilling of estuarine embayment by marine and fluviatile sediments (Powell and Martens 2005). An estimated 666,000 ha of ASS occur within the Great Barrier Reef (GBR) catchments of Queensland, Australia. Extensive areas have been drained causing acidification, metal contamination, deoxygenation and iron precipitation in reef receiving waters (Powell and Martens 2005).

Landfills

Historical **coastal landfills** are potential sources of diffuse pollution due to leaching of contaminants through groundwater. For example, the United Kingdom alone has approximately 20,000 historical landfill sites without engineered waste management and leachate control (e.g. Cooper et al. 2012). Many of the historical landfill sites around the Thames River, London are in low-lying, flood-prone areas and recent sampling of sediments showed Cu, Pb and Zn contamination from anthropogenic sources (O'Shea et al. 2018). These legacy sites are problematic but enhanced environmental regulations have halted uncontained landfill sites in many countries. There are risks of increased

landfill leachates impacting marine ecosystems in the future due to limited environmental regulatory controls or limited enforcement of them in some countries, although some mitigation reuse prospects for leachates are developing (Wijekoon et al. 2022). Cash-poor, low-and middle- income countries also accept (for a price) a large portion of the world's difficult-to-manage waste such as e-waste and known toxicants (e.g. Makam et al. 2018).

Desalination Plants

Desalination plants treat seawater to extract freshwater from the ocean. Metals are introduced to marine waters from desalination plants in waste brine with corrosion of metallic surfaces of the desalination system (e.g. Sadiq 2002) resulting in changes to community structure (Roberts et al. 2010). Desalination has become a reliable solution to water stress by supplying potable water in regions where freshwater supply is restricted. Some work is being done on brine management and pre-treatment to minimise the impacts of desalination from both brine and metal toxicity (Khan and Al-Ghouti 2021).

5.3 Metal Behaviour in Marine Waters

5.3.1 Metal Speciation

Metals enter aquatic systems in both dissolved and particulate forms. Of concern are the chemical species that make up these forms, their stability and possible transformations and transport that can occur over time. The chemical (and physical) speciation can be approached in several ways as will be discussed, but ultimately the concern is for their potential to cause biological effects to aquatic biota, i.e. their **bioavailability**, or potential to be taken up by aquatic organisms with the likelihood of toxic effects.

The speciation of dissolved metals in its simplest form involves the free metal ion, e.g. Cu²⁺, and metals that are complexed or bound to complexes, both inorganic (e.g. sulfate, carbonate) or organic (e.g. natural humic and fulvic acids or other anthropogenic organic contaminants) (e.g. Rashid 1985; Florence and Batley 1988; Allen 1993; Batley et al. 2004). Hydrous iron and manganese oxides form binding sites for many metals, particularly in estuarine waters where these exist as colloidal species, often in heterogeneous mixtures with organic complexes. In some instances, these forms aggregate and are transported to bottom sediments.

The greatest bioavailability has been shown to involve the free metal ion, whereas **complexes** with dissolved organics are considerably less bioavailable. It is typical to use the term **lability** to describe the ability of metal-organic complexes to dissociate at a biological membrane and exert toxic effects. Strong metal complexes are usually non-labile, whereas weak complexes are typically labile. Lability is, however, operationally defined, so measurements of the labile fraction determined using a particular technique need to be assessed for their link to toxicity to sensitive biota. Organometallic complexes such as methylmercury where the metal is covalently bound to a carbon atom, are usually lipid-soluble (unless charged) and are directly transported across biological membranes and so have greater toxicity than other complexed forms.

The bioavailability of metals in estuarine and marine waters will be controlled by pH, salinity and redox potential, together with the presence of dissolved organic matter and its metal-binding constant (Luoma 1996; Batley et al. 2004). Many metals can exist in solution in different oxidation states, in particular Fe, Mn, Cr, As and Se, and these have different bioavailabilities and toxicities. Often both oxidation states can co-exist with transformations between forms highly dependent on redox potential. Manganese is a typical example, where in oxic waters, it exists as colloidal MnO₂, whereas in anoxic waters, Mn²⁺ prevails. Since MnO₂, as with hydrous iron (III) oxides, is able to adsorb metals, redox potential changes can significantly affect this association.

Metal speciation and toxicity (particularly of Cu, Pb, Ni, Zn and Cd) in natural waters depend on the pH, and the type and concentration of potential complexing **ligands**. The tendency for metals to form certain complexes is largely pH-dependent. Because the pH is easily changed in freshwater a large range of complexes are possible (Turner et al. 1981). In contrast, seawater is well buffered at a pH of 8.1–8.2 (Sadiq 1992), and the range of complexes that can form is more limited compared to freshwater. Variations in pH occur in coastal and estuarine environments due to freshwater mixing (e.g. Riba et al. 2003), groundwater inputs (e.g. Santos et al. 2011), and interactions with floodplain soils (see acid sulfate soils in this chapter).

There are several extensive reviews of metal chemistry in marine and aquatic waters which discuss metal behaviour in detail (e.g. Batley 1989; Sadiq 1992; Tessier and Turner 1995). This section provides a basis to build your knowledge upon and the literature cited are good places to seek more detailed information.

Metal Complexation

Complexes in freshwater are formed predominantly by oxygen-containing ligands (nitrates, phosphates, sulfates and organic acids), whereas most metal complexes in seawater are chloro- and carbonate or bicarbonate complexes (Kester 1986). Cadmium and copper exhibit the most notable differences in their toxicities between fresh and salt water. Cadmium is considered to be an extremely toxic metal (Hawker 1990; Sadiq 1992; Baird and Cann 2012) and this is true in freshwater environments, where the chloride concentration is low, and cadmium forms complexes with oxygen-containing ligands. These cadmium oxo-complexes are more labile and more bioavailable. With the abundance of chloride in seawater, more thermodynamically stable cadmium complexes are formed, which may be less bioavailable. Conversely, copper in seawater forms more labile chloro- and carbonate complexes (Steemann Nielsen and Wium-Andersen 1970).

A reduction in salinity, due to freshwater influxes from rainfall can be extreme during major weather events. Reduced salinity may extend far offshore and remain for several weeks, interfering with the dominance of metal-chloride complexes and subsequently altering trace metal availability.

Many metal ions including Fe, Co, Ni, Cu, Zn and Cd, are complexed by organic ligands in seawater which influences their speciation. For iron, these include siderophores (low-molecular-weight ligands produced by marine bacteria), humic and fulvic substances and microbial exopolymeric substances (porphyrins, saccharides and humic-like substances), while for copper, protein-based phytoplankton exudates, thiols and humic substances appear to dominate (Sato et al. 2021).

The dissolved organic matter content of marine waters is very low except in areas close to river discharges where it is more abundant and the nutrient availability affects the abundance of planktonic masses. Planktonic and other biotic interactions have been reported to affect copper speciation due to the complexing capacity of the associated organic molecules (e.g. Jones and Thomas 1988; Florence and Batley 1988). Hence, large temporal and spatial variations in the copper complexing capacity of seawater are expected and may cause large variations in the speciation of copper in seawater (Coale and Bruland 1990; Sadiq 1992).

Metal Interactions with Suspended Particles

Adsorption to the surfaces of **suspended particles** plays an important role in the removal of metals from seawater. The capacity for metals to bind to these surfaces depends upon the size, composition and abundance of the particles, concentration of other ions in solution, the charge of the metal ion and pH of the solution. Metal adsorption onto suspended particles is a significant mechanism controlling their solubility and dispersion (Batley and Gardner 1978; Florence 1986; Sadiq 1992; Reichelt-Brushett et al. 2017b). **Flooding events** can transport suspended sediment and freshwater loads far offshore (e.g. Devlin and Schaffelke 2009).

Positive and negative charges can be present simultaneously on solid surfaces of colloidal particles. It is commonly supposed that the **adsorption of ionic species** occurs in response to attraction by solids of opposite electrical charge. However, this oversimplification does not take into account of adsorption of non-electrolytes, selectivity between ions of like charge, adsorption of ionic species on solids of like charge or the reversal of charge that occurs when an excess of certain ionic species is adsorbed (Parks 1975). The binding capacity of colloidal material to trace metals depends on the net charge density of the particle.

Clays carry both a positive charge and a negative charge, and the magnitude of the charge depends on the type of clay. Positive charges are a result of the isomorphous replacement of structural oxygen by the hydroxyl groups: this leaves a negative charge deficiency. Negative charges are largely due to the isomorphous replacement of the structural silicon by aluminium or ferric iron, or the replacement of structural aluminium by magnesium or ferrous iron (Yariv and Cross 1979). Negative charges on clays are usually more common than positive charges. Positively charged metallic exchangeable cations are adsorbed in the inter-layer spaces (Yariv and Cross 1979). The capacity of clay minerals to adsorb ions is primarily governed by the degree of electrostatic attraction or cation exchange capacity (CEC) (e.g. Gambrell et al. 1976; Davranche and Bollinger 2001), which shows a linear relationship with particle size (Ormsby et al. 1962). Hydroxides and hydrous oxides of polyvalent cations such as aluminium, iron and manganese often cover clay minerals and some are potentially able to attract positively charged metal ions or species from seawater (e.g. Drever 1982).

Despite humic compounds and clays both being negatively charged, they do not necessarily repel one another: organo-clays can form as a result of intricate and varied forms of bonding involving physical and chemical forces. The reaction involved depends on the nature of the humic material, the type of clay minerals, the ionic composition of seawater and pH conditions. The chemical bonds associated with the organo-clays influence trace metal adsorption and desorption from particles. Some of the most prominent bonds are ionic bonds, coordinate bonds or ligand exchange and hydrogen bonds.

5.3.2 Evaluating Metal Speciation and Bioavailability in Marine Waters

Geochemical Modelling

There are a range of geochemical models that have been used to estimate the **equilibrium speciation of dissolved metals** (Batley et al. 2004) and the findings are not necessarily consistent. A challenge remains with the accommodation of binding to colloids and to natural organic ligands. Modelled complexation of Cu^{2+} in seawater varies widely with different major species predicted (e.g. Kester (1986) suggested that 90% of copper in seawater forms carbonate complexes; Hawker (1990) 90% of copper in seawater is in the form of copper hydroxide; and Sunda and Hanson (1987) suggested that organic complexation plays a major role). While the outputs of such models are of interest, they provide little information about metal bioavailability.

The Biotic Ligand Model (BLM)

A major advance in identifying the bioavailable concentration of metals in natural waters was offered by the biotic ligand model (BLM) as an extension of the free ion activity model (Pagenkopf 1983). The BLM is based on the assumption that metal bioavailability and toxicity are controlled by the binding of metals to a fish gill or cell membrane surface via a biotic ligand (BL). There is competition for this ligand between the free metal ion, protons, other metal ions, and organically and inorganically bound metals. Application of the BLM requires a chemical speciation model and derived equilibrium constants for the metal-BL complexes. The BLM has been applied extensively to metals in freshwaters, but there have been limited applications to marine waters apart from that for copper (Arnold et al. 2005). Limitations to current approaches to marine waters have been discussed by de Polo and Scrimshaw (2012). BLM models usually only predict metal toxicity to within a factor of 2.

Speciation Measurement

Measurement techniques offer a dynamic approach to the estimation of metal bioavailability, compared to the equilibrium approaches offered by modelling. In essence, these involve the measurement of an **operationally defined labile metal fraction** that is able to be related to the bioavailable or toxic form. Measurement techniques, as described by Batley et al. (2004), include separations using a chelating resin, electroanalytical techniques such as anodic stripping voltammetry and the use of diffusive gradients in thin films (DGT) to sample a metal fraction that diffuses via a gel membrane to a chelating resin-binding phase.

Toxicity Testing

The ultimate test of whether the chemical species are in forms that are potentially toxic requires the use of a sensitive bioassay (\triangleright Chapter 3).

5.4 Metal Behaviour in Marine Sediments

5.4.1 Metal Forms in Sediments

Metals in sediments are distributed among a range of chemical forms. In particular, these include metals adsorbed to iron and manganese oxyhydroxides often in association with organic matter in stabilised colloids in





Figure 5.5 Conceptual model of major metal contaminant processes in sediments (where M indicates 'metal', POC is particulate organic carbon, and Org refers to organic compounds, so POC—Org is organics associated with POC). *Image*: Simpson, Stuart; Batley, Graeme, editors. Sediment quality assessment: A practical guide. CSIRO; 2016

surface waters, that ultimately aggregate and precipitate, particularly as the salinity increases to that of seawater, ultimately settling to bottom sediments. In anoxic waters, sulfides metals such as Cu, Cd, Ni, Pb and Zn form sulfides with low solubility products that will precipitate, thereby becoming enriched in marine sediments (Chester 1990). For this reason, sediments are referred to as a **sink** for metals with metals being most often found in higher concentrations in sediments than in marine waters at any particular site (Förstner 1987) (**2** Figure 5.5).

Typically, a zone of oxygenation extends from the sediment:water interface to about 1–5 cm below the sediment surface. This is known as the oxic zone. Below this is an intermediate sub-oxic zone of reduction overlying an anoxic zone, where dissolved oxygen is minimal and sulfate-reducing bacteria are active ($\$ Figure 5.6a). If reduced sediments, high in metals are mobilised, the sulfide is oxidised to sulfate and the associated metals can be released from the sediments into the water column. Bioturbation ($\$ Figure 5.6b–d) results in a mixing of the oxic and anoxic zones and benthic organisms can be in close contact with sediments, pore water (water that sits between sediment particles) and associated metals.

A number of selective extraction schemes have been devised to quantify the metal phases in sediments. These typically consider an exchangeable fraction, separate fractions for carbonates, organics (and sulfides) and metal oxyhydroxides, and a residual fraction comprising inert mineralised forms (Hass and Fine 2010). While these are useful for comparing sediments, the analytical techniques are operationally defined and not truly selective and, more importantly, they do not relate to metal bioavailability. Analysis of metals in sediments typically uses a total acid digestion, however, a cold, dilute acid extraction has been shown to best relate to the bioavailable fraction and discriminate from the mineralised forms. This will dissolve iron and manganese oxyhydroxides and metal sulfides (Simpson and Batley 2016).

5.4.2 Metal Bioavailability in Sediments

Sediment Grain Size

In the metric scale sediment grain size range from clays (<2 μ m diameter) to silts (2–<63 μ m) and sand (<63 μ m–2 mm). Gravel, rocks and other coarse material exceed 2 mm. Metal concentrations are highest in the finer clay and silt particles which have a greater surface area and hence more binding sites for metals. It is therefore important when reporting metal contamination to indicate the grain size. Most sediment quality guideline values apply to clay/silt sediments. The same metal concentration in a sandy sediment would potentially have greater bioavailability than that in a clay/silt sediment.

Pore Waters

Pore waters (or interstitial waters) are the waters occupying the spaces between sediment particles, typically comprising 30–80% of the sediment volume, depending



• Figure 5.6 Sediment redox interactions with organisms; a black reducing sediment just below the surface in a mangrove area. The aerial roots of mangroves are called pneumatophores and take up oxygen in these reducing sedimentary environments; b some fish such as a number of goby species excavate burrows to live in, sometimes they also share these burrows with shrimp who help in the excavation; c large sediments mounds (~25 cm diameter) processed by benthic organisms; d high-density benthic burrowers. *Photos* A. Reichelt-Brushett

on the grain size. Because they are in close association with sediments, porewater contaminants are in chemical equilibrium with those in sediments. Pore waters represent a diffusive pathway for metals to overlying waters. The speciation and bioavailability of porewater metals will be largely controlled by redox potential and pH. Burrowing organisms (Figure 5.6) can introduce oxygenated waters into anoxic sediments, oxidising iron and manganese and other metal sulfides and releasing metals that can diffuse to overlying waters. The changing physicochemical conditions associated with bioturbation influence metal bioavailability and toxicity.

Acid Volatile Sulfides (AVS)

In sub-oxic sediments, amorphous iron and manganese monosulfides, so-called **acid-volatile sulfides** (AVS) (because they dissolve in dilute acids) can react readily with dissolved metals (e.g. Cd, Cu, Ni, Pb and Zn) forming insoluble metal sulfides. This means that if there are metals in the sediments or pore waters that can exchange with AVS, then there should be no bioavailable metals, and hence no toxicity, provided AVS is in excess of the available exchangeable metals. The exchangeable metals (so-called simultaneously extractable metals (SEM)) and AVS are both measured after dilute acid extraction of the sediments to determine if AVS>SEM (Simpson and Batley 2016 and citations therein).

5.5 Metal Uptake by Marine Organisms

The topic of bioaccumulation of metals in marine biota is very broad. The general principles of bioaccumulation are provided in \blacktriangleright Chapter 3 and further details on measuring rates of accumulation are provided in \blacktriangleright Chapter 6. These same principles apply to metals but the ways in which they interact with biota need to be specifically considered given that some metals are essential in small quantities for life. Furthermore, metals generally do not biomagnify as they are not lipophilic (there are a few exceptions, such as mercury when it is methylated).

Metal uptake by organisms not only depends on metal chemistry in the different environmental compartments the organism utilises (water, sediment and biota) but also on the metal interactions within an organism (e.g. an organism's ability to take up, regulate and detoxify accumulated metals). Such abilities vary between taxonomic groups and the different life stages of a species. Some filter-feeding marine organisms such as bivalve molluscs have been utilised in biomonitoring studies of pollution because they readily bioconcentrate and bioaccumulate contaminants (see ► Chapter 2, Box 2.1).

Importantly, metal ion **assimilation** (the processes of uptake) is essential for organisms and the pathways of uptake and methods of regulation help to satisfy their dietary requirements of essential metals while avoiding **Metals and Metalloids**

toxicity, known as **homeostasis**. It is possible for some non-essential metals to be taken up via these pathways and also regulated. When metal concentrations exceed an organism's ability to store and regulate them, then the organism exhibits toxic responses (Morrison et al. 1989). Here, we discuss processes of metal uptake and methods of regulation.

5.5.1 Transport Across Biological Membranes

There are three main metal uptake pathways by which metals enter organisms. The simplest route is via passive diffusion where metals diffuse through aqueous pores in cell membranes. The rate of diffusion is a function of the size of the molecule with larger colloidal species excluded. Active transport is driven by potential ionic gradients across the membrane, known as membrane-bound ion channels and higher metal concentrations can overwhelm their function (Morrison et al. 1989). Metal uptake termed carrier-mediated transport is facilitated by carrier molecules that involve interaction with the cell membrane (Morrison et al. 1989; Rainbow et al. 1990; Riba et al. 2003). Additionally, siderophores, organic chemicals excreted by organisms such as phytoplankton and bacteria, complex metals in seawater which can then be taken across the membrane (Vraspir and Butler 2009). Once inside an organism, diffusible metal species are able to bind to non-diffusible, intracellular ligands, and may be transferred to blood proteins and transported away from the uptake site (Rainbow et al. 1990).

5.5.2 Other Uptake Routes

Examples of other ways that organisms may accumulate metals include **ingested from food sources** when metals are bound to ingested sediment particles, or directly in the food they consume.

Once metals are ingested by organisms, the internal body conditions may then play a role in changing the metal speciation, as seen in the pearl oysters *Pinctada carchariarium* in Shark Bay, Australia (McConchie and Lawrence 1991). Cadmium concentrations in these oysters exceeded health guidelines, but there was no apparent anthropogenic or geologic contamination of the environment. It was discovered that cadmium in the water had adsorbed onto fine particles of negatively charged colloidal hematite (Fe₂O₃). During normal filter-feeding, oysters ingested these metal-loaded particles, and the lower pH conditions in the gut of the oyster induced a reversal of the hematite charge which caused cadmium to be released from the particles (i.e. become bioavailable) and subsequently absorbed by the oysters.

5.5.3 Metal Detoxification

Some organisms are able to regulate metal uptake through detoxification processes such as sequestration in granules, or by temporary storage in granules that are later excreted or made available for use (Rainbow et al., 1990). Similarly, lysosomes are used by many invertebrates such as crustaceans to sequester metals (e.g. Sterling et al. 2007). Lysosomes are organelles that regulate cellular waste. Other organisms can regulate and detoxify metals through the production of metallothionein proteins which can be enhanced by increased metal loads (Roesijadi and Robinson 1994; Roseijadi 1996). Metallothionein proteins not only play a role in the homeostasis of essential metals such as copper and zinc but can also be induced by non-essential metals such as cadmium (Stillman et al. 1999). Another detoxification system used by some algae is the production of a layer of metal hydroxides such as Fe(OH)₃ on the outside of the cell which adsorbs metals and thus renders them less toxic.

Some elements can provide protection from toxicity of other metals. A rather well-known example of this is the protective effects that selenium (an essential element) seemingly plays with mercury for some marine mammals (e.g. Kehrig et al. 2016) and seabirds (e.g. Ikemoto et al. 2004). The presence of selenium reduces the availability of some metal ions by forming insoluble compounds (Feroci et al. 2005).

Processes of detoxification require energy that is diverted from other needs or organisms such as sourcing food, growth and reproduction.

5.5.4 Metal Depuration

Depuration is the process that removes metals from the organism's body and is helpful in understanding the longer term ability of organisms to regulate metal loads and recover from toxicity after exposure. Many studies on the uptake and toxicity of metals now incorporate a recovery phase where organism health is monitored for a period after the exposure to the toxicant has ended. Depuration can occur as a reverse of passive and active diffusions (► Section 5.4.1), in organism waste, shedding of exoskeletons, reproductive outputs (e.g. eggs, sperm and offspring) and suckling of young in marine mammals. Some pathways of depuration need to be considered in biomonitoring studies (► Box 5.3).

Box 5.3: Cautious Considerations for Using Some Species as Biomonitors

Caution needs to be taken for some species intended for use in biomonitoring studies and consideration of depuration pathways is important. For an interesting example, corals have often been considered useful as biomonitors because they are sessile, easy to collect and the same genetic colonies can be subsampled over time. However, corals and some other marine species such as anemones, jelly fish and giant clams, contain symbiotic dinoflagellates (Symbiodiniaceae). Some thoughts about using corals as biomonitors:

- when corals are stressed they may bleach resulting in a loss of the Symbiodiniaceae;

- gametes take place 5–9 months to develop and can amount to about 80% of the tissue weight of a coral; the time of
 year sampling takes places in relation to annual spawning will influence the contribution of the gametes to the overall
 sample mass;
- clear differences exist for different metals in terms of the uptake and partitioning between the coral tissue, symbiotic dinoflagellates, gametes and skeleton as summarised by Reichelt-Brushett and McOrist (2003) and further investigated in Hardefeldt and Reichelt-Brushett (2015); and
- the density of the dinoflagellates can naturally vary widely within and between colonies depending on factors such as
 exposure of the coral surface to sunlight, therefore repeated sampling of the same colony is unlikely to have consistent
 ratios of host tissue and dinoflagellates.

For the reasons above, each type of biological material should be assessed separately or at least their mass contribution to the sample taken into the consideration in the assessment (Figure 5.7).



G Figure 5.7 **b** Box 5.3: Metals in corals can be lost from the colony though bleaching, coral may recover from a bleaching event and will slowly regain Symbiodiniaceae; **a** coral bleaching; **b** clear linear assemblages of Symbiodiniaceae in *Acropora muricata*. *Photos*: A. Reichelt-Brushett

5.6 Metal Toxicity to Marine Organisms

Metals can affect many factors associated with the health of marine organisms and the mode of action (> Chapter 3) will vary between taxonomic groups. Table 5.4 provides a summary of the types of effects measured in organisms after exposure to metals. These responses have been measured in a combination of field and laboratory studies and specific responses have only been measured in some species (e.g. moulting is a typical feature of crustaceans but is not common in other taxa). Table 5.4 provides some insight into what might be useful organism responses to be measured. ured in future studies. Metal toxicity in marine waters and sediments can be considered in relation to the concentrations that cause detrimental effects and can be generally categorised in order of toxicity (• Table 5.5), although the order may vary depending on the environmental conditions as explained above. Values are based on the 95% species protection values except for the two metals that are known to biomagnify, mercury and cadmium, for which the 99% species protection value is recommended as default guideline values. The two metals, mercury and copper, that are among the greatest concern in marine waters in relation to toxicity and current sources will be discussed further. (content sourced from Weis 2014 and citations there in)

Response mechanisms	Examples of sublethal responses of organisms after metal exposure
Osmoregulation	Loss of osmoregulatory capacity through organ damage, inhibition of Na ⁺ , K ⁺ and ATPase inhibition
Excretion	Reduced ammonia excretion due to decreased food intake Increased ammonia excretion due to increased protein catabolism (digestion) Decreased excretion rates and faeces production
Respiration and metabolism	Enhanced or reduced respiration rates due to changes in enzyme activity Enhanced mucous production Reduced metabolism is a strategy to minimise metal uptake or a result of damage to organs such as gills Affects metabolic biomarkers (e.g. ATP, histidine)
Feeding	Growth can be inhibited due to reduced feeding which may be a manifestation of changed behaviour (e.g. bivalves may remain closed to avoid poor water quality)
Digestion	Inhibition of digestive enzymes
Reproduction and development	Endocrine disruption (impacting the nervous system and reproductive system) Reduced sperm motility and reduced fertilisation success Delayed moulting Delayed sexual maturity Reduced larval motility Interference with metamorphosis
Embryonic development	Reduced fecundity Inhibition of embryo development Failure to hatch Deformities Genotoxicity
Growth	Reduced growth Impaired limb regeneration Reduced pigment production Abnormal growth Weakened bones and reduced calcification Tumours
Behaviour	Disruption of mating activity Erratic swimming Increased swimming speed Decreased motility Lack of interest in optimal habitat Reduced valve closing speed in molluscs Active avoidance of contamination (e.g. reduced burrowing and burying in contaminated sed- iments) Decreased prey capture Reduced escape ability Reduced olfactory (food odour) responses Reduced response to water-borne alarm substances resulting in increased vulnerability to predators Retardation of schooling behaviour and migration Neurotoxicity

Table 5.4 Example of types of responses exhibited by marine biota when exposed to elevated metal concentrations in marine waters

Table 5.5 General order of metal toxicity in marine environments (based on Australian and New Zealand default guideline values (DGVs) for 95% species protection for marine waters (99% for Hg and Cd) and the related DGVs for sediments, expressed as molar concentrations. Available at: > https://www.waterquality.gov.au/anz-guidelines/guideline-values/default/water-quality-toxicants)

	General order of metal toxicity (most toxic first)
Marine water ^a	$TBT^b > Hg^c > Cd > Cu, Ag > Pb, Se > Cr(VI), Co > Ni, As > Zn > V > Cr(III)$
Marine sediments ^a	$TBT^b > Hg^c > Ag, Cd > As, Pb > Ni > Cu > Cr > Zn$

^a where metals are not shown, insufficient data exist, ^b as nM Sn/kg, ^c inorganic Hg

5

5.6.1 Mercury Toxicity to Marine Biota

Data on the acute toxicity of mercury (II) chloride (HgCl₂) in marine water to biota was summarised by the US EPA (1985) and values ranged from 3.5 to $1700 \,\mu$ g/L, depending on the species. Hg (II) concentrations ranging from 10 to 160 μ g/L inhibited growth and photosynthetic activity of marine plants (ANZECC/ ARMCANZ 2000). Wu and Wang (2011) showed that an inorganic mercury concentration between 15 and $36 \,\mu\text{g/L}$ inhibited the growth of three marine algae species, and effects from organometallic forms of mercury were similar but interspecies variations were evident. Marine molluscs are relatively resistant to the effects of mercury exposure, but some life stages are sensitive. Fertilisation success of the European clam (Ruditapes *decussatus*) was significantly reduced compared to controls at 32 μ g/L, the EC50 (EC50 is defined in \triangleright Chapter 3) for embryonic development was 21 µg/L, and larval survival was affected at 4 µg/L after 11 days exposure (Fathallah et al. 2010). Responses of crustaceans to mercury exposure can be variable. The proteasome systems (a protein complex which degrades unneeded or damaged proteins) of the lobster Homarus gammarus and crab Cancer pagurus were severely inhibited by mercury at concentrations of 2 and 5 mg/L respectively (Götze et al. 2014) but these concentrations are unlikely to be reached in the environment.

Dietary pathways of exposure to mercury are also an important consideration for toxicity. Mercury (II) exposure via the diet of post-larvae *Penaus monodon* after 96 h resulted in changed swimming behaviour and this endpoint was more sensitive than biochemical biomarker endpoints including glutathione S-transferase (GST) and acetylcholinesterase activity (AChE) (Harayashiki et al. 2016). Dietary exposure of inorganic mercury concentrations below 2.5 μ g/g to juvenile *P. monodon* for up to 12 days did not increase the body burden or impact AChE activity but resulted in a suppression of CAT activity at 2.5 μ g/g (Harayashiki et al. 2018).

Mercury is generally less toxic to fish than some other metals, such as Cu, Pb, Cd or Zn. The main danger is diet-derived methylmercury, which accumulates in internal organs and exerts its effects by disruption of the central nervous system. Harayashiki et al. (2019) studied the effects of dietary exposure to inorganic mercury on fish activity and brain biomarkers on yellowfin bream (*Acanthopagrus australis*) and found that swimming activity increased for the test population after dietary exposure to food containing 2.4 and 6 μ g/g although there was some variably between concentrations. Additionally, GST activity was also higher in mercury-exposed fish relative to controls, but differences were not found for other biomarkers.

Bioaccumulation of mercury from water may also be an issue. Bioconcentration factors of 5000 have been reported for mercury (II); factors for methylmercury ranged from 4000 to 85,000 (US EPA 1986). Further studies could focus on reproductive success resulting from maternally derived mercury to embryonic and larval stages.

5.6.2 Copper Toxicity to Marine Biota

EC10 values and no observed effect concentrations (NOECs) for the chronic effects of copper on marine algae range from $0.2-10 \mu g/L$ (ANZECC/ARMCANZ 2000) (examples provided in **D** Table 5.6). The acute toxicity of copper to marine animals is also wide-rang-

Table 5.6 Some examples of marine species' sensitivity to copper $(\mu g/L)$				
Species	Endpoint	Duration	EC10	Source
Algae				
Nitzschia closterium	Exponential growth	72 h	8	Johnson et al. (2007)
Phaeodactylum tricornutum	Exponential growth	72 h	1.5	Osborn and Hook (2013)
Echinoderms				
Evechinus chloroticus	Larval development	96 h	2.1	Rouchon (2015)
Corals				
Acropora aspera	Fertilisation success	5 h	5.8	Gissi et al. (2017)
Mollusc				
Mytilus galloprovincialis	Embryo development	48 h	5	Zitoun et al. (2019)
Haliotis iris	Larval development	96 h	0.7	Rouchon (2015)
Fish				
Sparus aurata	Juvenile growth	30 d	290 (NOEC)	Minghetti et al. (2008)
Atherinops affinis	Embryo development	12 d	62 (NOEC)	Anderson et al. (1991)

ing from 5.8 μ g/L for blue mullet to 600 μ g/L for green crab (US EPA 1986). Invertebrates, particularly crustaceans, corals and sea anemones are sensitive to copper. Fertilisation success is a sensitive endpoint for copper across a wide range of marine invertebrates. A good summary was provided by Hudspith et al. (2017), who reported that EC50 estimates ranged between 1.9 and 10,030 μ g/L, with most species of corals, echinoderms, polychaetes, molluscs and crustaceans tested exhibiting EC50 estimates of <70 μ g/L.

Gastropods seem to be more tolerant to copper and can accumulate quite high concentrations without toxic effects and typical 96-h LC50 values for snails are 0.8–1.2 mg Cu/L (ANZG 2018). Marine bivalves, including the mussel *Mytilus edulis* are more sensitive to copper, with a 96-h LC50 of 480 µg/L (Amiard-Triquet et al. 1986). Reduced growth and larval development were found at copper concentrations as low as 3 µg Cu/L in bivalves (ANZG 2018 and references therein).

Marine fish appear to be relatively tolerant of copper (ANZG 2018). In general, embryos of marine fish are more sensitive than their larvae, whereas larvae of freshwater fish are more sensitive than embryos.

5.7 Managing Metal Pollution

5.7.1 What Is 'Pollution'

Pollution is the introduction of harmful materials into the environment. These harmful materials are called pollutants. Many environmental scientists prefer the term contaminants as all pollutants are contaminants but not all contaminants are pollutants (see > Chapter 1 for further details). The challenge is in defining what level of contamination constitutes pollution. Metal concentrations that are close to guideline values are deemed contaminated, but we don't have an accepted metric that defines polluted or heavily contaminated. Nevertheless, it is common among the general public to refer to water pollution and air pollution as representing something bad that needs management. We need to keep that in mind when we are talking about mildly contaminated waters and say they are polluted, as it over-exaggerates the problem.

5.7.2 Guideline Values

Many countries have guideline values (or similar) to protect marine ecosystems from contaminants including metals in marine waters (● Table 5.7) and separate guidelines for sediments (see also ► Chapter 3). Some countries have also developed protocols to determine state/province or site-specific guidelines. The guideline values for waters are usually derived from rigorous toxicological testing, usually laboratory-based, using multiple aquatic species (e.g. Warne et al. 2018; ANZG 2018; Gissi et al. 2020). Most long-term guideline values are based on chronic toxicity testing, whereas short-term effects use acute toxicity data.

Chronic toxicity is defined as a lethal or adverse sub-lethal effect that occurs after exposure to a chemical for a period of time that is a substantial portion of the organism's life span (>10%) or an adverse effect on a sensitive early life stage. Acute toxicity is a lethal or adverse sub-lethal effect that occurs after exposure to a chemical for a short period relative to the organism's life span (Warne et al. 2018).

When chronic toxicity data are used in **species sen**sitivity distributions (SSDs) to derive guideline values, it is usual to apply the 95% species protection value to most waters, defined as slightly to moderately contaminated, while the more conservative 99% species protection value is reserved for high conservation value waters, e.g. in a national park (see ► Chapter 6 for further details in SSDs). Species protection levels of 90 and 80% are both reserved for highly disturbed ecosystems and it is these values that likely constitute pollution as the stated goal with such waters is a continual improvement (ANZG 2018; ANZECC/ARMCANZ 2000).

For sediments, guideline values are commonly based on the 10th percentile of a ranking of effects data (Simpson and Batley 2007, 2016). Limited approaches to the chronic toxicity testing of whole sediments have been undertaken, e.g. for copper (Simpson et al. 2011), hampered until recently by the availability of a sufficient number of whole sediment test species (Simpson and Batley 2016).

5.8 Summary

Most metals and metalloids are found naturally in the marine environment in very low concentrations and many are essential to life. Anthropogenic inputs from atmospheric emissions, mining, mineral processing and urban and industrial discharges increase the concentrations in marine environments. Coastal waters are at greater risk of predominantly terrestrially derived metal sources.

Each metal behaves differently and organo-metallic metal forms are generally the most toxic to marine organisms. Understanding the sediment and water interactions, chemical behaviour and pathways of metal uptake in marine organisms are important for understanding toxic effects. Toxic effects vary between different metals and are different for different taxonomic groups.

• Table 5.7 Examples of water quality guidelines and protocols used in different countries and how to access them		
	Country	Guideline name and access location
	Australia and New Zealand	Australian and New Zealand Guidelines for Fresh and Marine Waters www.waterquality.gov.au/anz-guidelines/guideline-values/default
	Canada	Canadian Water Quality Guidelines for the Protection of Aquatic Life www.ccme.ca/en/summary-table
	European Union	UK Technical Advisory Group, Water Framework Directive, Proposals for environmental quality standards for Annex VIII substances 2008
	USA	National Recommended Water Quality Criteria -Aquatic life https://www.epa.gov/wqc/national-recommended-water-quality-crite- ria-aquatic-life-criteria-table

5.9 Study Questions and Activities

- 1. Select one metal and describe the sources, fate and consequences in the marine environment. This may be a metal that is explored in the chapter, or you may select a different metal of interest to you. Use diagrams if you wish.
- Investigate the cycle and fluxes of a metal of environmental concern and explain it in your own words or create your own conceptual model (for an example see ► Box 5.1).
- 3. Investigate the guideline values for metals in marine waters in your region or country. What are three key points you notice about them in the context of this chapter?
- 4. What metal do you think is of most concern in the marine environment? Justify your answer.

References

- Adiansyah JS, Rosano M, Vink S, Keir G (2015) A framework for a sustainable approach to mine tailings management: disposal strategies. J Clean Prod 108:1050–1062
- Albarano L, Costantini M, Zupo V, Lofrano G, Guida M, Libralato G (2020) Marine sediment toxicity: a focus on micro- and mesocosms towards remediation. Sci Total Environ 708:134837
- Allen HE (1993) The significance of trace metal speciation for water, sediment and soil quality criteria and standards. Sci Total Environ 134:23–45
- Amiard-Triquet C, Berthet B, Metayer C, Amiard C (1989) Contribution to the ecotoxicological study of cadmium, copper and zinc in the mussel Mytilus edulis. Mar Biol 92:7–13
- Anderson BS, Middaugh DP, Hunt JW, Turpen SL (1991) Copper toxicity to sperm, embryos and larvae of topsmelt *Atherinops affinis*, with notes on induced spawning. Mar Environ Res 31:17–35
- Angel BM, Hales LT, Simpson SL, Apte SC, Chariton AA, Shearer DA, Jolley DF (2010) Spatial variability of cadmium, copper, manganese, nickel and zinc in the Port Curtis Estuary, Queensland, Australia. Mar Freshw Res 61:170–183
- ANZECC/ARMCANZ (Australian and New Zealand Environment Conservation Council/Agriculture and Resource Management Council of Australia and New Zealand). (2000) Australian and New Zealand guidelines for fresh and marine water quality. Canberra, Australia. Available at: ► https://www.waterquality.

gov.au/anz-guidelines/resources/previous-guidelines/anzecc-armcanz-2000. Accessed 12 Jan 2022

- ANZG (Australian and New Zealand Governments) (2018) Australian and New Zealand guidelines for fresh and marine water quality. Australian and New Zealand Governments and Australian state and territory governments, Canberra ACT, Australia. Available at: ▶ www.waterquality.gov.au/anz-guidelines. Accessed 14 Nov 2021
- Apte SC, Benko WI, Day GM (1995) Partitioning and complexation of copper in the Fly River, Papua New Guinea. J Geochem Explor 52:67–79
- Apte SC, Batley GE, Szymczak R, Rendell PS, Lee R, Waite TD (1998) Baseline trace metal concentrations in New South Wales coastal waters. Mar Freshw Res 49:203–214
- Apte SC, Day GM (1998) Dissolved metal concentrations in the Torres Strait and Gulf of Papua. Mar Pollut Bull 36:298–304
- Arnold WR, Santore RC, Cotsifas JS (2005) Predicting copper toxicity in estuarine and marine waters using the Biotic Ligand Model. Mar Pollut Bull 50:1634–1640
- Baird C, Cann M (2012) Environmental chemistry, 5th edn. W.H. Freeman and Company, New York, p 776
- Baker MC, Ramires-Llodra EZ, Tyler PA, German CR, Booetius A, Cordes EE, Dubilier N, Fisher CR, Levin LA, Metaxas A, Rowden AA, Santos RS, Shank T, Van Dover CL, Young CM, Watén A (2010) Biogeography, ecology, and vulnerability of chemosynthetic ecosystems in the deep sea. In: McIntyre A (ed) Life in the world's oceans: diversity, distribution, and abundance. Wiley-Blackwell, Chichester, p 384
- Barrie LA, Gregor D, Hargrave B, Lake R, Muir D, Shearer R, Tracey B, Bidleman T (1992) Arctic contaminants: sources, occurrence and pathways. Sci Total Environ 122:1–74
- Batley GE, Gardner D (1978) Copper, lead and cadmium speciation in some estuarine and coastal marine waters. Estuar Coast Mar Sci 7:59–70
- Batley GE (1989) Trace element speciation, analytical methods and problems. CRC Press Inc., Florida, p 360
- Batley GE (1987) Heavy metal speciation in waters, sediments and biota from Lake Macquarie, NSW. Aust J Mar Freshw Res 38:591–606
- Batley GE (2012) "Heavy metal"—A useful term. Integr Environ Assess Manag 8:215–215
- Batley GE, Apte SC, Stauber JL (2004) Speciation and bioavailability of trace metals in water: progress since 1982. Aust J Chem 57:903–939
- Batley GE, Simpson SL (2016) Introduction. In: Simpson S, Batley G (eds) Sediment quality assessment—A practical guide, 2nd edn. CSIRO Press, Clayton South, pp 1–14
- Becouze-Lareure C, Dembélé A, Coquery M, Cren-Olivé C, Bertrand-Krajewski J-L (2019) Assessment of 34 dissolved and particu-

late organic and metallic micropollutants discharged at the outlet of two contrasted urban catchments. Sci Total Environ 651:1810–1818

- Birch GF, Lean J, Gunns T (2015) Historic change in catchment land use and metal loading to Sydney estuary, Australia (1788–2010). Environ Monit Assess 187:594
- Brady JP, Ayoko GA, Martens WM, Goonetilleke A (2015) Development of a hybrid pollution index for heavy metals in marine and estuarine sediments. Environ Monit Assess 187:306
- Brandt A, De Broyer C, De Mesel I, Ellingsen KE, Gooday AJ, Hilbig B, Linse K, Thomas MRA, Tyler PA (2007) The biodiversity of the deep Southern Ocean benthos. Philos Trans R Soci Lond, Ser B, Biol Sci 362:39–66
- Breuer E, Stevenson AG, Howe JA, Carroll J, Shimmield GB (2004) Drill cutting accumulations in the Northern and Central North Sea: a review of environmental interactions and chemical fate. Mar Pollut Bull 48:12–25
- Brewer A, Dror I, Berkowitz B (2022) Electronic waste as a source of rare earth element pollution: leaching, transport in porous media, and the effects of nanoparticles. Chemosphere 287:132217
- Brown BE, Holley MC (1982) Metal levels associated with tin dredging and smelting and their effect on intertidal reef flats at Ko Phuket, Thailand. Coral Reefs 1:131–137
- Chapman PM (2007) Heavy metal—music, not science. Environ Sci Technol 41:6C
- Chapman PM (2012) "Heavy metal"—cacophony, not symphony. Integr Environ Assess Manag 8:216–216
- Chester R (1990) Marine geochemistry. Allen Unwin, Australia, p 698
- Cionek VM, Alves GHZ, Tófoli RM, Rodrigues-Filho JL, Dias RM (2019) Brazil in the mud again: lessons not learned from Mariana dam collapse. Biodivers Conserv 28:1935–1938
- Coale KH, Bruland KW (1990) Spatial and temporal variability in copper complexation in the North Pacific. Deep Sea Res Part a, Oceanogr Res Pap 37:317–333
- Cooper N, Bower G, Tyson R, Flikweert J, Rayner S, Hallas A (2012) Guidance on the anagement of landfill sites and land contamination on eroding or low-lying coastlines (C718). CIRIA. Classic House, London, p 174
- Davranche M, Bollinger J-C (2001) A desorption–dissolution model for metal release from polluted soil under reductive conditions. J Environ Qual 30:1581–1586
- de Polo A, Scrimshaw MD (2012) Challenges for the development of a biotic ligand model predicting copper toxicity in estuaries and seas. Environ Toxicol Chem 31:230–238
- De Vera J, Chandan P, Landing WM, Stupple GW, Steffen A (2021) Amount, sources, and dissolution of aerosol trace elements in the Canadian Arctic. ACS Earth and Space Chemistry 5(10):2686–2699
- Devlin M, Schaffelke B (2009) Spatial extent of riverine flood plumes and exposure of marine ecosystems in the Tully coastal region, Great Barrier Reef. Mar Freshw Res 60:1109–1122
- Drazen J, Smith C, Gjerde K, Haddock S, Carter G, Choy C, Clark M, Dutrieux P, Goetze E, Hauton C, Hatta M, Koslow A, Leitner A, Pacini A, Perelman J, Peacock T, Sutton T, Watling L, Yamamoto H (2020) Opinion: Midwater ecosystems must be considered when evaluating environmental risks of deep-sea mining. Proc Natl Acad Sci USA 117:17455–17460
- Drever JI (1982) The geochemistry of natural waters. Prentice-Hall, New Jersey, p 239
- Driscoll CT, Mason RP, Chan H-M, Jacob DJ, Pirrone N (2013) Mercury as a global pollutant: sources, pathways, and effects. Environ Sci Technol 47:4967–4983
- Echavarri-Erasun B, Juames JA, García-Castrillo G, Revilla JA (2007) Medium-term responses of rocky bottoms to sewage discharges from a deepwater outfall in the NE Atlantic. Mar Pollut Bull 54(7):941–954

- Etter RJ, Rex M, Chase MC, Quattro JM (1999) A genetic dimension to deep-sea biodiversity. Deep Sea Res I 46:1095–1099
- Fathallah S, Medhioub MN, Medhioub A, Kraiem MM (2010) Toxicity of Hg, Cu and Zn on early developmental stages of the European clam (*Ruditapes decussatus*) with potential application in marine water quality assessment. Environ Monit Assess 171:661–669
- Ferndez-Arcaya U, Drazen JC, Murua H, Ramierz-Llodra E, Bahamon N, Recasens L, Rotlant G, Company JB (2016) Bathymetric gradients of fecundity and egg size in fishes: a Mediterranean case study. Deep-sea Res 116:106–117
- Feroci G, Badiello R, Fini A (2005) Interactions between different selenium compounds and zinc, cadmium and mercury. J Trace Elem Med Biol 18:227–234
- Florence TM (1986) Electrochemical approaches to trace element speciation in waters: a review. Analyst 111:489–505
- Florence M, Batley G (1988) Chemical speciation and trace element toxicity. Chem Aust, pp 363–366
- Förstner U (1987) Sediment-associated contaminants -an overview of scientific bases for developing remedial option. Hydrobiologica 149:221–246
- Frainer G, Siciliano S, Tavares DC (2016) Franciscana calls for help: the short and long-term effects of Mariana's disaster on small cetaceans of South-eastern Brazil. In: Conference: International Whaling Commission. Bled, Slovenia Volume: SC/66b/SM/04
- Gaffney JS, Marley NA (2014) In-depth review of atmospheric mercury: sources, transformations, and potential sinks. Energy Emission Control Technol 2:1–21
- Gambrell RP, Kahlid RA Patrick WH Jr (1976) Physicochemical parameters that regulate mobilisation and immobilisation of toxic heavy metals. In: Proceedings of the speciality conference on dredging and its environmental effects. American Society of Civil Engineers, New York, pp 418–434
- Gerlach SA (1981) Marine pollution, diagnosis and therapy. Springer, Berlin, p 228
- German CR, Ramirez-Llodra E, Baker MC, Tyler PA (2011) Deep realm research beyond the census of marine life: a trans-Pacific road map. In: Oceans'11 MTS/IEEE, Kona, Waikoloa, HI, USA. Available at: ► https://ieeexplore.ieee.org/document/6106995. Accessed 13 Dec 2021
- Gissi F, Stauber J, Reichelt-Brushett A, Harrison P, Jolley DF (2017) Inhibition in fertilisation of coral gametes following exposure to nickel and copper. Ecotoxicol Environ Saf 145:32–41
- Gissi F, Wang Z, Batley GE, Leung KMY, Schlekat CE, Garman ER, Stauber JL (2020) Deriving a chronic guideline value for nickel in tropical and temperate marine waters. Environ Toxicol Chem 39:2540–2551
- Gladstone W (1996) Trace metals in sediments, indicator organisms and traditional seafoods of the Torres Strait. Final report of the Torres Strait baseline study. Great Barrier Reef Marine Park Authority, Townsville. Available at: ► https://elibrary.gbrmpa. gov.au/jspui/handle/11017/262. Accessed 15 Nov 2021
- Glover L, Earle S (eds) (2004) Defying ocean's end—An agenda for action. Island Press, Washington, p 250
- Götze S, Bose A, Sokolova IM, Abele D, Saborowski R (2014) The proteasomes of two marine decapod crustaceans, European lobster (*Homarus gammarus*) and edible crab (*Cancer pagurus*), are differently impaired by heavy metals. Comp Biochem Physiol Part C: Toxicol Pharmacol 162:62–69
- Gröger J, Proske U, Hanebuth TJJ, Hamer K (2011) Cycling of trace metals and rare earth elements (REE) in acid sulfate soils in the Plain of Reeds, Vietnam. Chem Geol 288:162–177
- Harayashiki CY, Reichelt-Brushett AJ, Butcher P, Lui B (2016) Behavioural and biochemical alterations in *Penaeus monodon* post-larvae diet-exposed to inorganic mercury. Chemosphere 164:241–247

- Harayashiki CAY, Reichelt-Brushett A, Butcher P, Benkendorff K (2018) Ingestion of inorganic mercury by juvenile black tiger prawn (*Penaeus monodon*) diet alters biochemical biomarkers. Ecotoxicology 27:1225–1236
- Harayashiki CAY, Reichelt-Brushett A, Benkendorff K (2019) Behavioural and brain biomarker responses in yellowfin bream (*Acanthopagrus australis*) after inorganic mercury ingestion. Mar Environ Res 144:62–71
- Hardefeldt J, Reichelt-Brushett A (2015) Unravelling the role of zooxanthellae in the uptake and depuration of an essential metal in *Exaiptasia pallida*; an experiment using a model cnidarian. Mar Pollut Bull 96:294–303
- Hauton C, Brown A, Thatje S, Mestre NC, Bebianno MJ, Martins I, Bettencourt R, Canals M, Sanchez-Vidal A, Shillito B, Ravaux J, Zbinden M, Duperron S, Mevenkamp L, Vanreusel A, Gambi C, Dell'Anno A, Danovaro R, Gunn V, Weaver P (2017) Identifying toxic impacts of metals potentially released during deepsea mining—A synthesis of the challenges to quantifying risk. Front Mar Sci 4:368
- Haynes D, Kwan D (2002) Trace metals in sediments from Torres Strait and the Gulf of Papua: concentrations, distribution and water circulation patterns. Mar Pollut Bull 44:1296–1313
- Hawker DW (1990) Bioaccumulation of metallic substances and organometallic compounds. In: Connell D (ed) Bioaccumulation of xenobiotic compounds. CRC Press, Boca Raton, pp 187–207
 Heffernan O (2019) Deep-sea dilemma. Nature 571:465–468
- Herrmann H, Nolde J, Berger S, Heise S (2016) Aquatic ecotoxicity of lanthanum—A review and an attempt to derive water and sediment quality criteria. Ecotoxicol Environ Saf 124:213–238
- Hass A, Fine P (2010) Sequential selective extraction procedures for the study of heavy metals in soils, sediments, and waste materials -a critical review. Crit Rev Environ Sci Technol 40:365–399
- Holdway DA (1992) Control of metal pollution in tropical rivers in Australia. In: Connell D, Hawker D (eds) Pollution in tropical aquatic systems. CRC Press, London, pp 231–246
- Howard IL, Vahedifard F, Williams JM, Timpson C (2018) Geotextile tubes and beneficial reuse of dredged soil: applications near ports and harbours. Proc Inst Civ Eng Ground Improv 171(4):244–257
- Howard P, Parker G, Jenner N, Holland T (2020) An assessment of the risks and impacts of seabed mining on marine ecosystems. Fauna and Flora International: Cambridge, United Kingdom, p 336. Available at: ► https://cms.fauna-flora.org/wp-content/ uploads/2020/03/FFI_2020_The-risks-impacts-deep-seabed-mining_Report.pdf. Accessed 14 Nov 2021
- Hudspith M, Reichelt-Brushett AJ, Harrison PL (2017) Factors affecting the sensitivity of fertilization to trace metals in tropical marine broadcast spawners: a review. Aquat Toxicol 184:1–13
- Ikemoto T, Kunito T, Tanaka H, Baba N, Miyazaki N, Tanabe S (2004) Detoxification mechanism of heavy metals in marine mammals and seabirds: interaction of selenium with mercury, silver, copper, zinc, and cadmium in liver. Arch Environ Contam Toxicol 47:402–413
- Johnson HL, Stauber JL, Adams MS, Jolley DF (2007) Copper and zinc tolerance of two tropical microalgae after copper acclimation. Environ Toxicol 22:234–244
- Jones GB, Thomas FG (1988) Effects of terrestrial and marine humics on copper speciation in an estuary on the Great Barrier Reef lagoon. Aust J Mar Freshw Res 39:19–31
- Khan M, Al-Ghouti MA (2021) DPSIR framework and sustainable approaches of brine management from seawater desalination plants in Qatar. J Clean Prod 319:128485
- Kehrig HA, Hauser-Davis RA, Seixas TG, Pinheiro AB, Di Beneditto APM (2016) Mercury species, selenium, metallothioneins and glutathione in two dolphins from the southeastern Brazilian coast: mercury detoxification and physiological differences in diving capacity. Sci Total Environ 186:95–104

- Kester DR (1986) Equilibrium models in seawater: applications and limitation. In: Bernhard M, Brinckman F, Sadler P (eds) The importance of chemical speciation in environmental processes. Spinger-Verlag, Berlin, pp 337–363
- Koekkoek B (2013) Measuring global progress towards a transition away from mercury use in artisanal and small-scale gold mining. M.A. Royal Roads University, Canada, p 74. ► https://viurrspace.ca/bitstream/handle/10170/567/Koekkoek_brenda.pdf?sequence=1&isAllowed=y. Accessed 8 Nov 2021
- Kress N, Herut B, Galil BS (2004) Sewage sludge impact on sediment quality and benthic assemblages off the Mediterranean coast of Israel -a long-term study. Mar Environ Res 57(3):213–233
- Lane TW, Morel MM (2000) A biological function for cadmium in marine diatoms. Proc Natl Acad Sci USA 97:4627–4631
- Lau S-L, Han Y, Kang J-H, Kayhanian M, Stenstrom MK (2009) Characteristics of highway stormwater runoff in Los Angeles: metals and polycyclic aromatic hydrocarbons. Water Environ Res 81(3):308–318
- Lent RM, Herczeg AL, Welch S, Lyons WB (1992) The history of metal pollution near a lead smelter in Spencer gulf, South Australia, Toxicol Environ Chem 36:139–153
- Luoma SN (1996) The developing framework of marine ecotoxicology: pollutants as a variable in marine ecosystems. J Exp Mar Biol Ecol 200:29–55
- Macleod C, Coughanowr C (2019) Heavy metal pollution in the Derwent estuary: history, science and management. Reg Stud Mar Sci 32:100866
- Makam AN, Puneeth MK, Varalakshmi, Jayarekha P (2018) E-waste management methods in Bangalore. In: Proceedings of 2nd international conference on green computing and Internet of Things, ICGCIoT, 6–10, 8572976
- Male Y, Reichelt-Brushett AJ, Pocock M, Nanlohy A (2013) Recent mercury contamination from artisanal gold mining on Buru Island, Indonesia—Potential future risks to environmental health and food safety. Mar Pollut Bull 77:428–433
- Marx AK, McGowan HA (2011) Long-distance transport of urban and industrial metals and their incorporation into the environment: sources, transport pathways and historical trends. In: Zereini F, Wisemand C (eds) Urban airborne particulate matter. Springer, Berlin, pp 103–126
- Maus V, Giljum S, Gutschlhofer J, da Silva DM, Probst M, Gass SLB, Luckeneder S, Leiber M, McCallum I (2020) A global-scale data set of mining areas. Sci Data 7:289
- McConchie DM, Lawrence IM (1991) The origin of high cadmium loads to some bivalve molluscs from Shark Bay, Western Australia: a new mechanism for cadmium uptake by filter feeding organisms. Arch Environ Contam Toxicol 21:1—8
- Mestre NC, Rocha T, Canals M, Cardoso C, Danovaro R, Dell'Anno A, Gambi C, Regoli F, Sanchez-Vidal A, Bebianno MJ (2017) Environmental hazard assessment of a marine mine tailings deposit site and potential implications for deep-sea mining. Environ Pollut 228:169–178
- Milinovic J, Rodrigues FJL, Barriga FJAS, Murton BJ (2021) Oceanfloor sediments as a resource of rare earth elements: an overview of recently studied sites. Minerals 11:142
- Minghetti M, Leaver MJ, Carpene E, George SG (2008) Copper transporter 1, metallothionein and glutathione reductase genes are differentially expressed in tissues of sea bream (*Sparus aurata*) after exposure to dietary or waterborne copper. Comp Biochem Physiol, c: Comp Pharmacol Toxicol 147:450–459
- Miranda LS, Marques AC (2016) Hidden impacts of the Samarco mining waste dam collapse to Brazilian marine fauna-an example from the staurozoans (Cnidaria). Biota Neotrop 16:e20160169
- NMM (National Maritime Museum) (2018) ► http://www.en.nmm. pl/underwaterarchaeology/wrecks-researched-by-nmm

- Montero N, Belzunce-Segarra MJ, Gonzalez J-L, Nieto O, Franco J (2013) Application of toxicity identification evaluation (TIE) procedures for the characterization and management of dredged harbor sediments. Mar Pollut Bull 71:259–268
- Morrison GMP, Batley GE, Florence TM (1989) Metal speciation and toxicity. Chem Br, pp 791–796
- Munawer ME (2018) Human health and environmental impacts of coal combustion and post-combustion wastes. J Sustain Min 17:87–96
- NAGD (2009) National assessment guidelines for dredging. Department of the Environment, Water, Heritage and the Arts, Commonwealth of Australia, Canberra, ACT
- Netherlands National Water Board (2008) Sacrificial anodes, merchant shipping and fisheries. Emission estimates for diffuse sources. Netherlands Emission Inventory. Available from
 http://www.emissieregistratie.nl/erpubliek/documenten/Water/ Factsheets/English/Sacrificial%20anodes,%20merchant%20shipping.pdf. Accessed 19 Nov 2021
- Nriagu JO (1989) A global assessment of natural sources of atmospheric trace metals. Nature 338:47–49
- Nriagu JO (1996) A history of global metal pollution. Sci, New Ser 272:223–224
- Ormsby WC, Shartsis JM, Woodside KH (1962) Exchange behaviour of kaolins of varying degrees of crystallinity. J Am Ceram Soc 45:361–366
- Osborn HL, Hook SE (2013) Using transcriptomic profiles in the diatom *Phaeodactylum tricornutum* to identify and prioritize stressors. Aquat Toxicol 138:12–25
- O'Shea FT, Cundy AB, Spenser KL (2018) The contaminant legacy from historic coastal landfills and their potential as sources of diffuse pollution. Mar Pollut Bull 128:446–455
- Pacyna JM, Pacyna EG (2001) An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environ Rev 9:269–298
- Pacyna JM, Sundseth K, Pacyna EG (2016) Sources and fluxes of harmful metals. In: Pacyna J (ed) Environmental determinants of human health. Springer, New York, pp 1–26
- Pagenkopf GK (1983) Gill surface interaction model for trace-metal toxicity to fishes: role of complexation, pH, and water hardness. Environ Sci Technol 7:342–347
- Pan K, Wang W-X (2012) Trace metal contamination in estuarine and coastal environments in China. Sci Total Environ 421– 422:3–16
- Parks GA (1975) Adsorption in the marine environment. In: Riley J, Skirrow G (eds) Chemical oceanography, vol 1, 2nd edn. Academic Press, London, pp 341–308
- Powell B, Martens M (2005) A review of acid sulfate soil impacts, actions and policies that impact on water quality in Great Barrier Reef catchments, including a case study on remediation at East Trinity. Mar Pollut Bull 51:149–164
- Proske U, Heijnis H, Gadd P (2014) Using x-ray fluorescence core scanning to assess acid sulfate soils. Soil Res 52:760–768
- Queiroz HM, Nóbrega GN, Ferreira TO, Almeida LS, Romero TB, Santaella ST, Bernardino AF, Oterob XL (2018) The Samarco mine tailing disaster: a possible time-bomb for heavy metals contamination? Sci Total Environ 637–638:498–506
- Rainbow PS, Phillips DJH, Depledge MH (1990) The significance of trace metal concentrations in marine invertebrates—The need for laboratory studies in accumulation strategies. Mar Pollu Bull 21(7):321–324
- Ramirez-Llodra E, Brandt A, Danovaro R, De Mol B, Escobar E, German CR, Levin LA, Martinez Arbizu P, Menot L, Buhl-Mortensen P, Narayanaswamy BE, Smith CR, Tittensor DP, Tyler PA, Vanreusel A, Vecchione M (2010) Deep, diverse and definitely different: unique attributes of the world's largest ecosystem. Biogeosciences 7:2851–2899

- Ramirez-Llodra E (2020) Deep-sea ecosystems: biodiversity and anthropogenic impacts. In: Banet C (ed) The law of the Seabed— Access, uses and protection of seabed resources. 90: Publications on Ocean Development, Brill, Nijhoff, pp 924–1922
- Rashid MA (1985) Geochemistry of marine humic compounds. Springer-Verlag, New York, p 380
- Rayment GE (2011) Cadmium in sugar cane and vegetable systems of northeast Australia. Commun Soil Sci Plant Anal 36:597–608
- Reichelt AJ, Jones GB (1994) Trace metals as tracers of dredging activities in Cleveland Bay—Field and laboratory study. Aust J Mar Freshw Res 45:1237–1257
- Reichelt-Brushett AJ, McOrist G (2003) Trace metals in the living and nonliving components of scleractinian corals. Mar Pollut Bull 46(12):1573–1582
- Reichelt-Brushett AJ (2012) Risk assessment and ecotoxicology— Limitations and recommendations in the case of ocean disposal of mine waste. Oceanography 25(4):40–51. ► https://doi. org/10.5670/oceanog.2012.66
- Reichelt-Brushett AJ, Stone J, Thomas B, Howe P, Clark M, Male Y, Nanlohy A, Butcher P (2017a) Geochemistry and mercury contamination in receiving environments of artisanal mining waste and identified concerns for food safety. Environ Res 152:407– 418
- Reichelt-Brushett AJ, Clark MW, Birch G (2017b) Physical and chemical factors to consider when studying historical contamination and pollution in estuaries. In: Weckström K, Saunders K, Gell P, Skillbeck G (eds) Applications of paleoenvironmental techniques in estuarine studies. Springer, Dordrecht, pp 239–276
- Reichelt-Brushett A, Hewitt J, Kaiser S, Kim RE, Wood R (2022) Deep seabed mining and communities: A transdisciplinary approach to ecological risk assessment in the South Pacific. Integr Environ Assess Manag 18(3):664–673
- Riba I, García-Luquea RE, Blasco J, DelValls TA (2003) Bioavailability of heavy metals bound to estuarine sediments as a function of pH and salinity values. Chem Speciat Bioavailab 15:101– 114
- Rijkenberg MJA, Middag R, Laan P, Gerringa LJA, van Aken HM, Schoemann V, de Jong JTM, de Baar HJW (2014) The distribution of dissolved iron in the west Atlantic Ocean. PLoS ONE 9:e101323
- Roberts DA, Johnston EL, Knott NA (2010) Impacts of desalination plant discharges on the marine environment: a critical review of published studies. Water Res 44:5117–5128
- Roberts TL (2014) Cadmium and phosphorous fertilizers: the issues and the science. Procedia Eng 83:52–59
- Rogowska J, Wolska L, Namieśnik J (2010) Impacts of pollution derived from ship wrecks on the marine environment on the basis of s/s "Stuttgart" (Polish coast, Europe). Sci Total Environ 408:5775–5783
- Rogowska J, Kudłak B, Tsakovski S, Gałuszka A, Bajger-Nowak G, Simeonov V, Konieczka P, Wolska L, Namieśnik J (2015) Surface sediments pollution due to shipwreck s/s "Stuttgart": a multidisciplinary approach. Stoch Env Res Risk Assess 29:1797–1807
- Roesijadi G (1996) Metallothionein and its role in toxic metal regulation. Comp Biochem Physiol, Part C 113:117–123
- Roesijadi G, Robinsonson WE (1994) Metal regulation in aquatic animals: mechanisms of uptake, accumulation and release. In: Malins D, Ostrander K (eds) Aquatic toxicology: molecular, biochemical and cellular perspectives. CRC/Lewis Publishers, Boca Raton, pp 387–420
- Rouchon A (2015) Effects of metal toxicity on the early life stages of the sea urchin Evechinus chloroticus. Ph.D. thesis, Victoria University of Wellington, Wellington: New Zealand, p 211
- Rudnicka-Kępa P, Zaborska A (2021) Sources, fate and distribution of inorganic contaminants in the Svalbard area, representative

of a typical Arctic critical environment-a review. Environ Monit Assess 193:724

- Sadiq M (1992) Toxic metal chemistry in the marine environment. Marcel Dekker, New York, p 390
- Sadiq M (2002) Metal contamination in sediments from a desalination plant effluent outfall area. Sci Total Environ 287:37–44
- Saedi A, Jamshidi-Zanjani A, Khodadadi Daran A (2021) A review of additives used in the cemented paste tailings: environmental aspects and application. J Environ Manage 289:112501
- Salam MA, Dayal SR, Siddiqua SA, Muhib MI, Bhowmik S, Kabir MM, Rak AALE, Srednicki G (2021) Risk assessment of heavy metals in marine fish and seafood from Kedah and Selangor coastal regions of Malaysia: a high-risk health concern for consumers. Environ Sci Pollut Res 28:55166–55175
- Santos IR, Glud RN, Maher D, Erler D, Eyre B (2011) Diel coral reef acidification driven by porewater advection in permeable carbonate sands, Heron Island, Great Barrier Reef. Geophys Res Lett 38:L03604
- Sato M, Ogata N, Wong KH, Obata H, Takeda S (2021) Photodecomposition of natural organic metal-binding ligands from deep seawater. Mar Chem 230:103939
- Saunders JK, Fuchsman CA, KcKay C, Rocap G (2019) Complete arsenic-based respiratory cycle in the marine microbial communities of pelagic oxygen-deficient zones. Proc Natl Acad Sci USA 116:9925–9930
- Schneider L, Maher W, Potts J, Gruber B, Batley G, Taylor A, Chariton A, Krikowa F, Zawadzki A, Heijnis H (2014) Recent history of sediment metal contamination in Lake Macquarie, Australia, and an assessment of ash handling procedure effectiveness in mitigating metal contamination from coal-fired power stations. Sci Total Environ 490:659–670
- Scwartzendruber P, Jaffe D (2012) Sources and transport—A global issue. In: Banks M (ed) Mercury in the environment—pattern and processes. University of California Press, London, pp 3–18
- Shelley RU, Sedwick PN, Bibby TS, Cabedo-Sanz P, Church TM, Johnson RJ, Macey AI, Marsay CM, Sholkovitz ER, Ussher SJ, Worsfold PJ, Lohan MC (2012) Controls on dissolved cobalt in surface waters of the Sargasso Sea: comparisons with iron and aluminum. Glob Biogeochem Cycles 26:GB2020
- Simpson S, Batley G (2007) Predicting metal toxicity in sediments: a critique of current approaches. Integr Environ Assess Manag 3:18–31
- Simpson SL, Batley GE, Hamilton IL, Spadaro DA (2011) Guidelines for copper in sediments with varying properties. Chemosphere 75:1487–1495
- Simpson S, Batley G (2016) Sediment quality assessment—A practical guide, 2nd edn. Clayton South, CSIRO Press, p 346
- Stauber JL, Adams MS, Batley GE, Golding L, Hargreaves I, Peeters L, Reichelt-Brushett A, Simpson S (2022) A generic environmental risk assessment framework for deep-sea tailings placement using causal networks. Sci Total Environ 845:157311
- Steelman Neilsen E, Wium-Andersen S (1970) Copper ion as poison in the sea and freshwater. Mar Biol 6:93–97
- Steinberg PD, Airoldi L, Banks J, Leung KMY (2016) Special issue on the World Harbour Project—Global harbours and ports: different locations, similar problems? Reg Stud Mar Sci 8:217–370
- Sterling KM, Mandal PK, Roggenbeck BA, Ahearn SE, Gerencser GA, Ahearn GA (2007) Heavy metal detoxification in crustacean epithelial lysosomes: role of anions in the compartmentalization process. J Exp Biol 210:3484–3493
- Stillman MJ, Green AR, Gui Z, Fowle D, Presta PA (1999) Circular dichroism, emission and EXAFS studies of Ag(I), Cd(II), Cu(I), and Hg(II) binding to metallothioneins and modeling the metal binding site. In: Klaassen C (ed) Metallothionein IV. Birkhauser Verlag, Basel, pp 23–35
- Sunda WG, Hanson AK (1987) Measurement of free cupric ion concentration in seawater by ligand competition technique involv-

ing copper sorption onto $\rm C_{18}$ SEP-PAK cartridges. Limnol Oceanogr 32:537–551

- Tarbuck EJ, Lutgens FK (1987) The Earth—An introduction to physical geology. Merrill Publishing Company, Ohio, p 590
- Tessier A, Turner D (eds) (1995) Metal speciation and bioavailability in aquatic systems. Wiley, Chichester, p 679
- Thorne RJ, Pacyna JM, Sunddetth K, Paycyna EG (2018) Fluxes of trace metals on a global scale. In: DellaSala D, Goldstein M (eds) Encyclopedia of the Anthropocene. Elsevier, Waltham, pp 93–103
- Trapasso G, Chiesa S, Freitas R, Pereira E (2021) What do we know about the ecotoxicological implications of the rare earth element gadolinium in aquatic ecosystems? Sci Total Environ 781:146273
- Turner DR, Whitefield M, Dickson AG (1981) The equilibrium speciation of dissolved components if freshwater and seawater at 25 °C and at one atmosphere pressure. Geochim Cosmochim 45:855
- Turner DR, Hassellov I-M, Ytreberg E, Rutgersson A (2017) Shipping and the environment: smokestack emissions, scrubbers and unregulated oceanic consequences. Elementa: Sci Anthropocene 5:45
- Tsventnenko YB, Black AJ, Evans LH (2000) Development of marine sediment reworker tests with Western Australian species for toxicity assessment of drilling mud. Environ Toxicity 15:540– 548
- US EPA (United States Environmental Protection Agency) (1985) Ambient water quality criteria for mercury—1984. Criteria and Standards Division, US Environmental Protection Agency, Washington, Report No. EPA-440/5-85-026. Available at: ► https://www.epa.gov/sites/default/files/2019-03/documents/ambient-wqc-mercury-1984.pdf. Accessed 23 Nov 2021
- US EPA (United States Environmental Protection Agency) (1986) Quality criteria for water. US Department of Commerce, National Technical Information Service, Springfield, PB87-226759, EPA 440/5 86-001. Available at: ▶ https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table. Accessed 23 Nov 2021
- Vare L, Baker M, Howe J, Levin L, Neira C, Ramirez-Llodra E, Reichelt-Brushett A, Rowden A, Shimmield T, Simpson S, Soto E (2018) Scientific considerations for the assessment and management of mine tailing disposal in the deep sea. Deep-sea tailing deposition: what is at risk? Front Mar Sci 5:17
- Veiga MM, Baker RF (2004) Protocols for environmental and health assessment of mercury released by artisanal and small-scale gold miners. GEF/UNDP/UNIDO Global Mercury Project, Vienna, p 289. Available at: ▶ https://delvedatabase.org/resources/protocols-for-environmental-and-health-assessment-of-mercury-released-by-artisanal-and-small-scale-gold-miners. Accessed 8 Nov 2021
- Velasquez-Lopez PC, Veiga MM, Hall K (2010) Mercury balance in amalgamation in artisanal and small-scale gold mining: identifying strategies for reducing environmental pollution in Portovelo-Zaruma, Ecuador. J Clean Prod 18(3):226–232
- Vraspir JM, Butler A (2009) Chemistry of marine ligands and siderophores. Ann Rev Mar Sci 1:43–63
- Warne MStJ, Batley GE, van Dam RA, Chapman JC, Fox DR, Hickey CW, Stauber JL (2018) Revised method for deriving Australian and New Zealand water quality guideline values for toxicants—Update of 2015 Version. Prepared for the revision of the Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Governments and Australian state and territory governments, Canberra, p 48. Available at: ▶ https://www.waterquality.gov.au/anz-guidelines/ guideline-values/derive/laboratory-data. Accessed 24 Nov 2021
- Washburn TW, Turner PJ, Durden JM, Jones DO, Weaver P, Van Dover CL (2019) Ecological risk assessment for deep-sea mining. Ocean Coast Manag 176:24–39

- Weis JS (2014) Physiological, developmental and behavioural effects of marine pollution. Springer, Dordrecht, p 452
- Wijekoon P, Arundathi Koliyabandara P, Cooray AT, Lam SS, Athapattu BCL, Vithanage M (2022) Progress and prospects in mitigation of landfill leachate pollution: risk, pollution potential, treatment and challenges. J Hazard Mater 421:126627
- Wu Y, Wang W-X (2011) Accumulation, subcellular distribution and toxicity of inorganic mercury and methylmercury in marine phytoplankton. Environ Pollut 159:3097–3105
- Yanchinski S (1981) Who will save the Caribbean? New Sci 92:388-389
- Yariv S, Cross H (1979) Geochemistry of colloidal systems, for Earth scientists. Springer-Verlag, New York, p 449
- Yoklavich MM, Greene HG, Cailliet GM, Sullivan DE, Lea RN, Love MS (2000) Habitat associations and deep-water rockfishes a submarine canyon: an example of a natural refuges. Fish Bull 98:625–641
- Zaborska A, Siedlewicz G, Szymczycha B, Dzierzbicka-Głowacka L, Pazdro K (2019) Legacy and emerging pollutants in the Gulf of Gdańsk (southern Baltic Sea)—Loads and distribution revisited. Mar Pollut Bull 139:238–255
- Zitoun R, Clearwater SJ, Hassler C, Thompson K, Albert A, Sander S (2019) Copper toxicity to blue mussel embryos (*Mytilus galloprovincialis*): the effect of natural dissolved organic matter on copper toxicity in estuarine waters. Sci Total Environ 653:300– 314

Open Access This chapter is licensed under the terms of the Creative Commons Attribution 4.0 International License (> http://creativecommons.org/licenses/by/4.0/), which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license and indicate if changes were made.

The images or other third party material in this chapter are included in the chapter's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the chapter's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

