1 Introduction

Box 1.1 Definitions

arsenate The arsenate ion AsO_4^{3-} is the common form in which arsenic is dissolved in oxygenated aquatic ecosystems. The arsenic in arsenate is arsenic 5, with an oxidation state of 5.

arsenite The arsenite ion AsO_3^{3-} is a dissolved form of arsenic, less common in aquatic ecosystems than arsenate but more toxic. Arsenic is in the form of arsenic 3, a more reduced oxidation state than As 5.

biomagnification Accumulation via trophic transfer of a metal to a higher tissue concentration in a predator than occurred in its prey occupying a lower trophic level in a food chain. Biomagnification is not a general principle of the food chain transfer of metals in inorganic form, but will occur in the case of the trophic transfer of organometals such as methyl mercury. Biomagnification is a general principle of the food chain transfer of organic contaminants.

biosphere That part of the Earth and its atmosphere which is inhabited by living organisms.

ecotoxicity Toxic effect of a chemical upon populations, communities and ecosystems.

ecotoxicology Study of the toxicological effects of chemicals upon populations, communities and ecosystems, integrating ecology and toxicology.

essential metal A trace metal required in very small doses for the functioning of the metabolism of an organism.

galvanization Process of applying a protective zinc coating to iron or steel.

heavy metal Term often used loosely without strict definition to refer to metals that interact in small doses with organisms to produce toxic effects. Definitions may refer to metals with a specific gravity greater than 4 or even greater than 5. Such definitions, however, would include some metals in Groups 1 and 2 of the Periodic Table which are not generally included in lists of 'heavy metals', implying some expected chemical characteristics of the metal in question.

major (metal) ion Ion of sodium, potassium, calcium or magnesium, present in high concentrations in all biological systems.

metal An element which is shiny and of high density, is malleable and ductile, is a good conductor of heat and electricity and usually enters chemical reactions as a positively charged ion.

metalloid An element with chemical properties between those of a metal and a non-metal, as defined by its position in the Periodic Table, for example arsenic.

microgram (µg) One millionth of a gram (10^{-6}g).

non-essential metal A trace metal for which no requirement for the functioning of the metabolism of an organism has been shown.

organometal A bound combination of a metal and an organic entity. Examples are methyl mercury, tetra-ethyl lead and tributyl tin.

Periodic Table An arrangement of the chemical elements in order of their atomic number, such that elements with similar chemical properties occur at regular intervals and fall into groups of chemically related elements.

ppb Abbreviation for 'parts per billion'. Typically used to express the amount of metal dissolved in water, for example micrograms per litre (µg/L).

ppm Abbreviation for 'parts per million'. Typically used to express the amount of metal per unit (usually dry) weight in organisms, often expressed in micrograms per gram (µg/g) or milligrams per kilogram (mg/kg), or of the amount of metal dissolved in water, for example micrograms per millilitre (µg/ml) or milligrams per litre (mg/L).

rare earth elements (lanthanides) Fifteen elements with atomic numbers 57 (lanthanum) to 71 (lutetium), widely used as industrial catalysts.

trace metal Term often used loosely without strict definition with the implication that the metal is present in only 'trace' concentrations. Where defined, a concentration limit of 0.01% (100 parts per million, ppm) may be quoted, although this limit is often exceeded by the concentrations of many 'trace metals' in different organisms. Some authors will apply the term 'trace metal' only to essential metals. Here the term 'trace metal' is used to include metals and metalloids that have the potential to be toxic to organisms at low doses, whether essential or non-essential.

1.1 Metals

Prologue. The widely used labels 'heavy metals' and 'trace metals' are difficult to define, not least because the variably included elements show a continuum of chemical and biological characteristics. The term 'trace metal' is used here to cover a wide range of metals and metalloids that typically occur in low concentrations in organisms and are potentially toxic, whether or not they are essential or non-essential.

Metals are familiar to all of us. At least most are. We know about iron, tin, zinc and many others, including mercury, the only metal to exist in elemental form as a liquid at room temperature. Metals are elements, and being elements they have the ability to form compounds with other elements. For example, rust basically consists of iron oxide – a compound formed by the reaction of iron with oxygen. Gold and platinum, on the other hand, are relatively inert. They do not form compounds very readily and stay in elemental metal form for eons, the

very property that makes them 'precious' and suitable for use in coinage and jewellery. Most metals, however, do not stay in elemental form and exist as compounds.

Many simple inorganic compounds of metals will dissolve in water, separating into ions, for example positive sodium ions and negative chloride ions in the case of salt. These ions can be present in the environment around us, dissolved in the water of soils, sediments, streams, rivers, seas and oceans. Yet, the compounds formed by metals are not always simple salts made up of two inorganic ions. Metals may bind with organic compounds such as proteins that make up much of our bodies, and indeed the organic material of all living organisms. Thus, iron is bound with a relatively complicated organic molecule to make up haemoglobin, which will bind reversibly with oxygen and carbon dioxide in our blood, delivering oxygen to tissues for use to generate energy and removing the resulting waste product, carbon dioxide.

So what defines a metal? This is such an apparently simple question, but one that is almost impossible to answer with objective certainty. What define a metal are its physical and chemical characteristics. There is a definition – metals are elements which are shiny and of high density, are malleable and ductile, are good conductors of heat and electricity and usually enter chemical reactions as positively charged ions. The appearance of 'usually' should already warn us that not all is straightforward. The Periodic Table lists all the elements, classifying them on the basis of their atomic structure, which is inevitably linked to their chemical properties. While different distinct groupings of elements with similar chemical properties can be recognised in the Periodic Table, in some regions of the table chemical properties may show relatively little change between adjacent elements. Thus different elements show the defining characteristics of metals to different extents. There is even a term, metalloid, for elements that show some but not all of the properties of a metal. For example, arsenic and antimony are regularly referred to as metalloids (or even sometimes semimetals), and occasionally aluminium and selenium may be included in this category. Of the 90 elements occurring naturally on Earth, most (67) might be considered to be metals.

Two labels for metals commonly occur when discussing interactions between metals and organisms. These are the terms 'heavy metals' and 'trace metals'. It is difficult enough to define a metal. It is even more difficult to provide a consistent, objective definition for each of these two collective terms.

The term 'heavy metal' has historically often been used to refer to those metals that are considered environmental pollutants. To be a pollutant, a metal would be toxic to organisms and thus have an ecotoxicological effect on biological communities. To be toxic, a metal would need chemical properties that mean that it binds to the wrong molecules in an organism – in the wrong place, at the wrong time, disrupting normal metabolism. And yet, 'heavy' implies that these metals share a common property of high physical density. Thus definitions of heavy metals refer to metals with a specific gravity greater than 4, or even greater than 5, with no reference to chemical properties. Furthermore, such a definition based on weight would include heavy elements such as radium, the actinides (naturally occurring radioactive elements) and the lanthanides (rare earth elements), elements that are not usually considered to be 'heavy metals'. The term 'heavy metal' is avoided here.

The term 'trace metal' is also difficult to pin down. By implication, it is a metal present in trace amounts in the environment, and some definitions include an upper concentration limit of 0.01% by dry weight (equivalent to 100 parts per million or $\mu g/g$) in an organism. This definition would encompass most of the metals commonly referred to as trace metals, although, as we shall see later in this book, there are spectacular examples of much higher concentrations in particular organisms of metals typically called trace metals. Furthermore, the term 'trace' is also sometimes used with the implication that the element is required in the metabolism of living organisms, in effect is an 'essential' element, a supposition not included in the definition based on environmental concentrations. We shall come to the question of essentiality in more detail shortly, but it

Table 1.1 **Selected trace metals and their abbreviations.**

Aluminium (Al)	Mercury (Hg)
Antimony (Sb)	Molybdenum (Mo)
Arsenic (As)	Nickel (Ni)
Cadmium (Cd)	Platinum (Pt)
Chromium (Cr)	Selenium (Se)
Cobalt (Co)	Silver (Ag)
Copper (Cu)	Tin (Sn)
Gold (Au)	Titanium (Ti)
Iron (Fe)	Tungsten (W)
Lead (Pb)	Vanadium (V)
Manganese (Mn)	Zinc (Zn)

remains the case that other authors include both essential and non-essential metals as 'trace metals' (Luoma and Rainbow, 2008).

There are chemical definitions of different categories of elements including metals based on their chemical problems that avoid the unsatisfactory terms 'heavy metals' and 'trace metals', but the knowledge of chemistry required to use such definitions is probably more than we need to assume here. This book is concerned with the metals that interact with living organisms in small amounts, all of which are toxic above a given threshold, while many of these same toxic metals are essential to life at lower concentrations. Many of them are the metals that have been mined in the British Isles for centuries, even thousands of years in the cases of copper and tin, often with ecotoxicological consequences on the surrounding vegetation and animal life. In order not to invent another collective term, the term 'trace metals' will be used here, stressing that, while some are essential metals and others non-essential, all are potentially toxic. Table 1.1 lists these trace metals. The list includes the so-called metalloids arsenic and antimony, and their part-time colleagues, aluminium and selenium. Apologies to those seeking better chemical categorisations, but pragmatism prevails here.

Absent from the list are other metals that are also required for life, typically in ionic form and referred to as the major metal ions. These major ions are the ions of sodium, potassium, calcium and magnesium. They are present in organisms in relatively high concentrations and do not exert toxic effects as do trace metals by binding inappropriately to disrupt metabolic pathways.

1.2 Metals and Humans

Prologue. Humankind has mined and smelted metals since the Bronze and Iron Ages for the production of artefacts that include tools, weapons and jewellery. Today, the various physical and chemical properties of the different metals concerned underpin technological development in many industries. Yet there has been a price to pay as particular metals of high ecotoxicity such as mercury and cadmium have been released into the environment with deleterious effects on the local biota, including humans.

From early history, humankind has recognised that metals can be used to advantage, and for eons metals have been mined to serve mankind's purposes. The very names Bronze Age and Iron Age highlight the importance to our ancestors of the development of the technology to enable the smelting of metal-rich ores to release their metals for the production of artefacts.

The Bronze Age is a period of history characterised by the use of copper initially, and then bronze, the alloy formed wholly or chiefly of copper and tin, to make tools, vessels and weapons. The addition of tin to copper yields a product that is more easily melted and better suited for casting. Bronze is also harder than copper. The pure copper stage (the Chalcolithic Age) of the Bronze Age goes back to about 5000 BC. Bronze first came on the scene in about 3500 BC, and the copper mines of Cyprus ('copper island') later contributed significantly to the booming trade of the Bronze Age world of the Mediterranean. In Bronze Age Britain, prehistoric humans were fashioning copper and then bronze tools from about 2500 to 800 BC. The largest Bronze Age copper mine in Northwest

Europe was on the Great Orme in north Wales, with peak activity between 1900 and 1600 BC (MacGregor, 2010). The copper and tin mines of Cornwall were also of worldwide importance. Cornish tin in particular was used in the production of a considerable proportion of the bronze objects made in the second millennium BC. Some of the early bronze objects also contained some arsenic in combination with copper and tin, resulting in a harder alloy. As we shall see in Cornwall, arsenic often occurs as an impurity in copper ores. Its initial incorporation into bronze, therefore, may have occurred by accident, but later arsenic-bearing minerals were intentionally added during smelting.

Bronze continues to be used today, for example in coinage (often with the addition of zinc) and in bearings, typically as phosphor bronze. The addition of phosphorus increases strength and hardness.

The technological availability of another metal, iron, brought the Bronze Age to an end, and the Iron Age began. The Iron Age was the final technological stage in the Stone–Bronze–Iron Age sequence, beginning in about 1200 BC. Iron replaced the more brittle bronze in implements and weapons. Iron had been used as a scarce and precious metal earlier, but the development of metallurgical techniques to smelt iron now allowed the exploitation of iron ore deposits, which are more widespread and plentiful than those of copper ores. During the first millennium BC, the ancient world rapidly converted to using iron for the manufacture of tools and weapons. While the Iron Age, for the first time, put weapons into the hands of many with inevitable consequences, the Iron Age also allowed the development of the iron plough and promoted consequent changes in agricultural procedures and indeed structures of society.

Iron is one of the most abundant elements on the Earth. While the Earth's core is largely metallic iron, in the Earth's crust, iron has reacted with many other elements, not least oxygen, to produce iron-rich minerals, including ores with the potential for technological and commercial exploitation after smelting.

Smelting is the process of the extraction of a metal from its ore. Smelting uses heat and an agent (typically carbon in the form of coke or charcoal) to decompose the ore, the carbon binding with any oxygen in the ore mineral to release elemental metal. Limestone is often added to remove final impurities, a process known as fluxing, leaving behind slag, a glassy mass usually containing a mixture of metal oxides and silicon dioxide. Thus, iron is typically extracted by heating iron ore with coke and limestone in a blast furnace to produce cast iron or pig iron. Steel is an alloy of iron with a small amount of carbon (0.1–2.1%), and this alloy is at the root of the infrastructure of our industrialised society today. Alloy steels contain additional elements such as manganese, nickel, chromium, molybdenum, titanium and vanadium, added to modify the characteristics of the steel.

Before the start of the Bronze Age, defined by the smelting initially of copper, then the production of bronze itself, two other metals, lead and tin, were the first metals to be smelted. The smelting of these two metals is relatively simple, the heat of a wood fire being sufficient to release the elemental metals from some ores. Cast lead beads date from about 6500 BC. Lead, however, is too soft to be used in construction or weapon manufacture, and its technological impact at the time was low. On the other hand, lead is easy to cast and shape, and its day came later when it was used extensively for the piping and storage of water (giving its name to 'plumbing'), and the sheathing of the wooden hulls of boats, by the ancient Greeks and Romans. The Romans had another use for lead, using lead acetate, known as sugar of lead, as a sweetener for wine, with potential toxic effects on heavy consumers. In the eighteenth century in Britain, Devonshire colic affected cider drinkers in the West Country, an affliction identified to be lead poisoning caused again by the addition of sugar of lead to sweeten the cider, and also by the use of lead linings in the cider presses. The toxicity of lead is not a health concern restricted to ancient or recent history. Lead-based paints commonly contain lead in the form of lead chromate (chrome yellow) or lead carbonate (white lead), but they are a health hazard, and sale to the general public in the United Kingdom was banned in 1992. Red lead (lead oxide) is used in the production of batteries, lead glass and rust-proof primer paints. Lead is widely used in roofing. In this

elemental form, lead cannot enter biological systems and is not toxic. Lead is also still widely used today in lead–acid batteries, originally invented in 1859. These batteries are particularly popular in the automobile industry, for they are able to supply high surge currents as required by starter motors.

In the twentieth century, an organic compound of lead, tetra-ethyl lead, known as antiknock, was widely added to petrol to prevent pre-ignition and increase a fuel's octane rating. As the fuel was consumed, lead was released into the atmosphere attached to fine particles or aerosols, providing the potential for the uptake of toxic lead into biological systems, including humans, with subsequent neurotoxic effects. Legislation in most (but not all) parts of the world, including Europe and the United States, has now banned the addition of lead to fuel. This banning has had another positive effect. It has allowed the expanded use of catalytic converters on vehicles to reduce the emission of toxic pollutants such as hydrocarbons, carbon monoxide and oxides of nitrogen, the lead in antiknock previously having acted as a catalyst poison, inactivating the converter by forming a coating on the catalyst.

Ores of tin were less common than those of lead, and tin is a soft, weak metal only marginally harder than lead. Therefore, as a pure metal, tin had even less technological impact in prehistory than lead, its significant contribution being its key role in the development of bronze. Tin does, however, have a well-known use today, giving its very name to sealed containers that preserve their food contents. In 1795, Nicholas Appert of Paris discovered that foodstuffs boiled in glass bottles and immediately sealed would keep for several months, thereby providing a solution to Napoleon Bonaparte's publicised problem of keeping food fresh for his troops on their marches (Alexander and Street, 1951). This discovery led to others, and Peter Durand, an Englishman, patented the process of sealing food in containers of iron covered with a thin film of tin, so preventing rust. The coating of iron with tin was not in itself novel, for tinned iron had been used in Bavaria in the thirteenth century for decorative articles and for parts of armour (Alexander and Street, 1951). The product of coating

iron or steel with tin is known as tinplate. Tinplate does not rust and has been used in huge quantities for the production of tin cans to hold preserved foods or other biodegradable products.

In the second half of the twentieth century, an organic compound of tin, tributyl tin (TBT), rose to prominence as a wide spectrum biocide given its very toxic nature. TBT was particularly used as an antifouling agent in the marine environment in the expectation that it would be broken down very quickly in the sea after release from antifouling paint. In the 1970s, however, it was realised that TBT was actually having severe ecotoxicological effects on non-target organisms in the sea, such as oysters and dogwhelks (in the latter case at remarkably low concentrations), and the use of TBT as an antifouling agent is now banned in many countries across the world (Luoma and Rainbow, 2008).

Today, copper makes a very important contribution to our technology in its own right. Copper is very ductile and malleable, is corrosion resistant, and has very high conductivities for electricity and heat. Thus copper wiring has underpinned the electrical industry, and copper piping is used extensively in plumbing. Another alloy of copper is brass, this time with zinc in various proportions according to the ductility and malleability desired. Brass is used for decoration given its bright appearance, and its low frictional properties make it fit for use in doorknobs, locks, gears, bearings, valves and ammunition casings. Brass also has acoustic properties that make it suitable for the production of musical instruments, with a section of an orchestra named after it. Copper has long been used to make coinage, typically in some variation of bronze. The Romans did at times use pure copper in coins, but more usually the coins of lower denomination were made of bronze. In Britain, copper was also used for humbler coinage until 1860, when bronze was substituted (Alexander and Street, 1951). This 'bronze' actually contained zinc as well as tin and copper, until the days of decimalisation. Today, the decimal coins are made of copper-plated steel, nickel-plated steel and alloys of copper and nickel (cupro-nickel) or nickel and brass. The biocidal properties of copper are reflected in its widespread use today in

antifouling paints. Before the development of antifouling paints, metallic copper itself was used to sheathe the hulls of boats, beginning in the eighteenth century. The copper sheathing, as in the case of the less effective lead sheathing used by the Romans, was required for protection of the hull, not only against surface-fouling organisms slowing down a vessel by disrupting flow over the hull, but particularly against wood-boring marine animals such as shipworms, destroying wooden hulls by their extensive burrowing.

The use of zinc in brass and coinage has been introduced earlier, but zinc also has other uses. Zinc has been used for roofing but its major use has been in the process of galvanisation – the coating of iron or steel with zinc, primarily to prevent corrosion, particularly in the automobile industry. Zinc is also a key ingredient in batteries, including general-purpose zinc–carbon batteries and heavy-duty zinc chloride batteries, which have been used to power the likes of torches, toys, clocks and transistor radios for a 100 years or so. Zinc–air batteries can be very small, as used in hearing aids, larger for use in cameras or very large to power electric vehicles.

Another metal, nickel, is similar to iron in some of its properties, with a high melting point and greater strength and hardness. On the other hand, nickel is strongly resistant to corrosion and can be used to electroplate iron, brass and silver. Being corrosion resistant and of attractive colour, electroplated nickel silver (EPNS) is common in tableware. Nickel is used today chiefly in alloys, as in the nickel–copper and nickel–brass alloys used in coinage, but particularly in nickel–steels, the addition of nickel providing increased hardness, strength and resistance to wear. Nickel is yet another metal used in batteries, originally in combination with cadmium in rechargeable nickel–cadmium batteries. These, however, have now been replaced by nickel–metal hydride batteries, involving mixtures of many different and often uncommon trace metals and rare earth elements.

Gold is the classic precious metal, being very resistant to corrosion. It is so chemically unreactive that it can be found in elemental form as nuggets, as veins in rock or as grains in alluvial sediments. Since gold is also the most malleable and ductile of metals while being relatively rare, it has long been used in the production of jewellery and other culturally valuable artefacts. In 1833, near the town of Mold in north Wales, a gold cape was discovered that was eventually dated back to about 2000 BC in the Bronze Age (MacGregor, 2010). The cape had been made with great skill from a single sheet of very thin gold. It may have originated from elsewhere in the Bronze Age world, and its occurrence in north Wales may be related to the presence of a major trading centre associated with the local Great Orme copper mine (MacGregor, 2010).

Pure gold is, however, too soft to be used alone in artefact production, and other metals are added for hardening, thereby defining the 'carat' qualities of gold jewellery today. A carat is a 24th part, and so 22 carat gold has 22 parts of pure gold by weight, and two parts of other alloy metals. In 22 carat gold jewellery, silver and copper together will make up the final two parts of the 24, while in gold coins it is often copper alone. Eighteen carat gold is popular in jewellery, for this alloy mixture is relatively serviceable and robust without too much loss of colour. White golds are also alloys of gold with other metals, usually nickel or palladium in sufficient amount to make the final product white. The corrosion resistance of gold and its rarity have also meant that it has been used in coinage since the first millennium BC. Gold previously played a fundamental role as a 'standard' in monetary systems, predominantly in the nineteenth century, and today central banks continue to keep a portion of their monetary reserves as gold bullion. Gold does also have practical technological uses, for example in electronics, as an alloy with mercury to form an amalgam for dentistry or as a protective coating on other metals (gold plating).

Platinum is even more corrosion resistant than gold and is one of the rarest elements on Earth. It is therefore a desirable precious metal for use in jewellery. In spite of its high cost, platinum does have applications where corrosion resistance is a top priority, and it is used in catalytic converters, electrical systems and medical equipment.

Silver is also used as a precious metal in jewellery in its own right, as well as historically being used in

coinage. Silver is relatively resistant to corrosion, but not to the extent of gold. Indeed, the burning of sulphur-containing gas in the home can lead to the blackening of silver objects as a result of the reaction of silver with oxides of sulphur. So-called silver coins usually contain alloys of silver with other metals such as copper, nickel and zinc, and often now contain no silver at all. Even 'sterling silver' contains 7.5% of other metals, usually copper, because pure silver is generally too soft for the production of functional objects such as cutlery and tableware. Nevertheless, the corrosion resistance of silver has led to its wide employment historically in the brewing and milk industries to line vats. Silver also has very high heat and electrical conductivities, hence its use in electrical conductors, and it is also used in mirrors. Large amounts of silver were required by the photographic industry in the form of silver nitrate used to develop films, until so much of the domestic market was replaced by digital photography.

Chromium is another metal used in electroplating, usually being deposited on nickel to increase hardness and durability. While chromium is used to contribute hardness to alloy steels, it is also the key ingredient of stainless steel. Stainless steel by definition resists corrosion and is widely used in cutlery, for example. Stainless steel contains at least 10.5% of chromium. The chromium is vital, for it binds with oxygen in the air to form a passive film of chromium oxide. This film then prevents access of the oxygen to the iron component of the steel to form rust. Salts of chromium have been used as pigments in paints since the 1800s, for example chrome yellow (lead chromate) and chrome red (lead chromate mixed with lead oxide), and also in glass manufacture. Other key industrial applications of chromium include the use of chromium salts to tan leather and as wood preservatives.

Cobalt is mainly used as a component of magnetic, high-strength, wear-resistant alloys, as in turbines. Its compounds, such as cobalt aluminate (cobalt blue), are used as blue pigments in paints and glass. Manganese is present in nearly all steels and in aluminium alloys, improving resistance to corrosion. Manganese is also used in the manufacture of batteries, manganese dioxide being a key component in zinc-carbon

batteries. Molybdenum is another trace metal added to alloy steels, particularly in combination with nickel and chromium, and molybdenum disulphide is used as a high-temperature, high-pressure lubricant. Titanium is a low-density metal with a very high strength-to-weight ratio and very good corrosion resistance. It is therefore used widely to produce strong lightweight alloys in military, aerospace, medical, sporting goods and other industries. Titanium dioxide is used as a catalyst and in the production of white pigments. Tungsten is the metal used classically in the filaments of incandescent electric light bulbs. Being very hard and of high density, tungsten is used in military projectiles for increased penetration, and in drill bits. Vanadium is also used in alloy steels, and vanadium pentoxide is a catalyst in the industrial production of sulphuric acid.

Mercury is the only metal to exist as a liquid at room temperature and is very volatile. Mercury is arguably the most toxic of all metals, a very potent neurotoxin, and can enter biological systems in dissolved form, in food or when breathed in. In sediments in the environment, inorganic mercury can be converted by bacteria into the organic compound methyl mercury (an organometal) which readily crosses biological membranes. Methyl mercury can also be biomagnified up aquatic food chains to reach bioaccumulated concentrations of toxicological concern in top predators, such as long-lived tuna. Biomagnification describes the accumulation via trophic transfer of a metal to a higher tissue concentration in a predator than occurred in its prey occupying a lower trophic level in a food chain. Biomagnification is not a general principle of the food chain transfer of metals in inorganic form, but will occur in the case of the trophic transfer of organometals such as methyl mercury.

The neurotoxic nature of mercury has long been recognised, as for example in the depiction of the 'mad hatter' in Lewis Carroll's *Alice in Wonderland*, written in 1865. Beaver fur was used in the nineteenth century in Britain to make good-quality top hats, while rabbit fur was used for cheaper hats. In the case of rabbit fur, however, it was necessary to treat the fur with mercury nitrate to roughen the fibres so that they

would mat well. Beaver fur has naturally serrated edges and did not require such mercury treatment. Beaver fur was, however, scarce and therefore expensive, so alternative furs were used. As a result, hatters breathed in toxic mercury fumes with neurotoxic consequences, including aberrant behaviour. Mercury is used in batteries, thermometers, barometers, mercury switches and fluorescent lamps. Other metals, such as tin, silver and gold, will dissolve in liquid mercury to form amalgams widely used in dentistry. In most cases, there is now social and environmental pressure to phase out industrial uses of mercury, simply because of its high toxicity and ecotoxicity.

Cadmium is another notoriously toxic trace metal, with previous industrial uses being phased out for this reason. Cadmium was used in nickel-cadmium batteries, but these are now obsolescent as they are replaced by better performing nickel–metal hydrid batteries. Cadmium was also used for corrosion-resistant plating on steel. Cadmium compounds have been used to stabilise plastics and as pigments, as in the cases of yellow cadmium sulphide and cadmium selenide, known as cadmium red. A new modern application has been the use of cadmium telluride in solar panels. Cadmium is not commonly commercially mined for its own sake, but as a by-product, for example in the exploitation of zinc sulphide ores.

The very word arsenic is synonymous with poison for many of us, and indeed arsenic is one of the more toxic trace metals. In the nineteenth century, arsenical pigments were in demand to colour cotton fabrics and wallpapers, and arsenic was also used in the making of glass, the manufacture of shot and fireworks and the tanning of leather. Its high toxicity also led to the use of arsenic in pesticides and herbicides, but such applications are now declining. Today, arsenic does have industrial uses, as it can be added to copper alloys such as bronze for strengthening, and it is employed in semiconductor manufacture.

Of other trace elements to be considered in this book, selenium is used as a pigment to colour ceramics and glass, and also as a decolouriser in glass-making to remove the green tint resulting from iron impurities. Selenium is also a semiconductor and is used in photocells, particularly thin-film solar cells of increasing importance for renewable energy production. Antimony is used in alloys with tin and lead and in lead-acid batteries, and antimony trioxide is used as a flame retardant in clothing, seat covers and toys.

While there is debate as to whether aluminium can be called a trace metal, given that it is the third most common element on Earth, after oxygen and silicon, it is included here because aluminium ecotoxicity can be significant. As a metal, aluminium has a remarkably low density, and aluminium alloys are vital to the aerospace, automobile and construction industries. Aluminium is also used in drink cans.

Late in the twentieth century, the industrial use of a new manmade form of metals exploded, with an inevitable subsequent appearance in the environment with potentially ecotoxicological effects. Nanoparticles are particles of between 1 and 100 nanometres in diameter, and many contain one or more trace metals. While they may occur naturally, as in the emissions of volcanoes, many forms of metal-containing nanoparticles are being manufactured for specific industrial and commercial purposes (Yon and Lead, 2008), usually exploiting their high surface area to volume ratios, which make the nanoparticles very reactive or catalytic. Common metal-containing nanoparticles include titanium dioxide nanoparticles used in sunscreens, cosmetics and paints, and silver-rich nanoparticles used in washing machines and clothing, such as socks, to kill bacteria and reduce odours. Gold nanoparticles are used in medicine for drug delivery and are also important in the optical electronic industry. Quantum dots are nanoparticles made of semiconducting materials and are therefore also used in the electronics world. One such quantum dot contains a double load of toxic trace metals, consisting of cadmium and selenium, with potential ecotoxicological concern on release of both into the environment.

While the release of toxic metals by humans into the environment from mining activities has been with us for thousands of years, the release of metal-rich nanoparticles in industrial and domestic effluents is a new and expanding source of

toxic trace metals into the environment. We shall see in this book how habitats and biological communities cope with the toxic challenge of trace metals in the environment, however novel their source.

1.3 Sources and Global Cycles of Metals

Prologue. What was the origin of metals on Earth? How do metals enter the biosphere, and how are they subsequently distributed by biogeochemical cycling? Humankind has disturbed such cycling, not least by changing the different rates of flux of particular metals between different environmental components of the Earth to cause the presence of an excess of an ecotoxic metal at a particular location at a particular time.

The early Universe consisted almost entirely of the element hydrogen, with perhaps some helium present. Other elements were subsequently formed by nuclear fusion. A series of nuclear fusion reactions results in the formation of elements up to the atomic mass (56) of iron, but the formation of heavier elements by nuclear fusion requires higher temperatures than are found in stars. These heavier elements are formed by the addition of neutrons into the atomic nucleus, and iron remains one of the most abundant elements in stars. Suns were formed by the gravitational collapse of parts of a molecular cloud called a nebula. Most of the collapsing mass coalesced into a central sun, but the remaining material made up a protoplanetary disc from which planets, moons and asteroids were formed, producing a solar system.

Our solar system, and therefore the Earth, formed 4.55 billion years ago, as the protoplanetary disc cooled and elements reacted with each other to form complex materials, eventually producing lumps of solid matter. Today the Earth has an onionlike structure with a core, mantle, crust and atmosphere, but originally it was probably a homogeneous ball of matter, later forming a series of layers of decreasing density outwards as it cooled. The high-density central core is composed mainly of iron and nickel, solid in the centre but liquid in the outer core. The mantle is mostly solid rock, but is in slow viscous motion over geological time. It contains a wide array of elements, including metals. The crust above the mantle is also solid rock formed by the cooling of the original molten magma. The Earth's crust, together with the outermost mantle, is made up of rigid plates (tectonic plates) which glide over the underlying parts of the mantle, driven by the convection currents therein carrying heat from the Earth's interior to nearer the surface. These tectonic plates move apart, for example along mid-ocean ridges. The emerging hot mantle material forms new rock, often in the form of lava from erupting volcanoes. Along mid-ocean ridges, the new crust formed at the bottom of the sea is actually widening the ocean, as in the case of the Atlantic. The introduction of new mantle material at the bottom of the sea brings with it a supply of metals from below. As mantle material is emitted under the sea, a cycle may be set up where sea water is drawn down through faults or porous sediments to be emitted again at very high temperatures (up to 465°C), but now rich in trace metals such as iron, copper and zinc, together with sulphide. It was late in the twentieth century that it was appreciated that these hydrothermal vents were home to spectacular biological communities, based on the primary production of organic matter by bacteria carrying out chemosynthesis using locally abundant sulphides as an energy source, as opposed to the more familiar primary production of organic matter by photosynthesising plants harnessing light energy in most ecosystems on Earth. While tectonic plates are pushed apart at spreading centres, there are complementary subduction zones where a tectonic plate is forced below its neighbour, typically associated with earthquakes and volcano activity.

During the cooling of the Earth, the molten rocks solidified at the surface to produce the crust. Over time, water emitted from the mantle condensed to form the oceans, leaving thicker parts of crust protruding above as the continents. The continents shared tectonic plates with their adjacent portions of thinner oceanic crust, and therefore were carried along in the several cycles of plate subduction and formation that have occurred during the history of the Earth. Mountain ranges are produced by continental