Mining Industry Pollutants

Chemical characteristics and their potential risks

Introduction

The continuous growth of population and increased global consumption of minerals and metals as a result of raised standards of living are increasing the demand for raw material and ores. This is particularly so for the metals and resources used in the high-technology industries, even in low- and middle-income countries (Öko-Institut e.V., 2007; International Council on Mining & Metals, 2012). Given the development of newer and better high-technology products, a broader range of elements are now used. For instance, in the semiconductor industry, 12 elements were used in 1980. By the 21st century, the number of elements used in this sector had increased to 60 (see Appendix Figure 5). This has resulted in an additional rise in demand as well as an increase in pressure on resources (Theis, 2007). Data about the acquisition of primary minerals and metals from mining are difficult to come by. However, in the USA alone, about 85.4 million tonne of primary metals and 294 million tonne of industrial minerals were mined in 2010 (Matos, 2012). Because of these increased demands for raw material, the interest in resource-rich low- and middle-income countries is increasing.

In general, most of the metals and metalloids are used in the industrial sector (in electronics, construction, and in the production of iron), and in the jewelry industry. Because of the increase in demand, the primary exploitation of these essential ores and minerals will further increase over time, while their natural stocks will decline. For instance, the natural stocks of rare earth elements (yttrium, niobium, neodymium, and scandium), the platinum group elements (platinum and palladium), the metalloid germanium, the transition metals (tungsten, cobalt, and molybdenum), the alkali metal lithium, the alkaline earth metal magnesium, and the metals tin and indium have been severely reduced (vbw, 2011). In contrast, the natural stocks of other metals, such as silver, gold, cadmium, manganese, zinc, and iron, have been less exhausted.

Different mining techniques are available for the primary extraction of metals. There are mainly two approaches – surface mining and underground mining. For surface mining, soil and rocks are blasted out of the subsoil or vegetation is removed to create open pits which lay bare the different ores and minerals. For underground mining, tunnel systems are created to exploit the minerals and ores. In general, open-pit mining is used more frequently (two-thirds of the time) than underground mining, because it is cheaper and less dangerous for the employees to work at the surface rather than in narrow underground shafts (Farrell et al., 2004; Blacksmith Institute and Green Cross, 2012).

During the mining, processing, and trade of primary minerals and metals there are four steps. These are ore and mineral exploitation, transportation, extraction, and refining. Several impacts of environmental concern are associated with these processes.

Impact of ore exploitation

The processing of mineral ores produces high volumes of waste. As the more high-grade ore deposits are diminished, lower-grade ones are used and even more waste is produced. For instance, the production of 0.3 mg of gold results in 79 tonne of mine waste. The production of 1 tonne of copper results in 110 tonne of tailings (waste ore) and 200 tonne of waste rocks (Farrell et al., 2004). [Note that the exploitation of mining commodities used as energy resources, such as fossil fuels (gas, oil, and coal) and radioactive uranium ore, and their risks to environmental and human health are not discussed in our report. This does not mean that they are less relevant or of less environmental concern: we did not have the resources to focus on these commodities as well.]

Open-pit mining produces higher amounts of waste than underground mining.

Generally for open-pit mining, higher amounts of waste are produced than from underground mines. This is because open-pit mining can be used to obtain lower-grade sediments and rocks from which the mineral can be extracted (United States Environmental Protection Agency, 1995). Open-pit mining is associated with deforestation and the consequent increased erosion of soil. It is also associated with the use of explosives – mixtures of ammonium nitrate and fuel oil, trinitrotoluene, and nitroglycerine – that may have adverse effects on environmental and human health by polluting vulnerable ecosystems (Brüning et al., 1999; Wihardja, 2010; Swenson et al., 2011; Butler, 2012).

Impact of transportation

In general, the exploited material is stockpiled in heaps or dumps to await further processing. To transport the material, trucks, conveyers, and railways are used. Because of that, hydraulic oils, fuels, lubricants (with such constituents as glycol ethers, benzene, ethylbenzene, toluene, and other hydrocarbons), and batteries (with sulfuric acid, lead, antimony, and arsenic) are needed. Some of these products may be released or dumped into the environment as well (United States Environmental Protection Agency, 1995).

Gold, silver, and platinum are often processed by leaching the heaps with cyanides or by amalgamation. The amalgamation process using mercury is especially of high environmental concern because large quantities of mercury are required and released into the environment during this process.

Impact of ore extraction

Beneficiation methods are used to extract and enrich the compounds of interest. These methods differ for different metals. Commonly, gravity concentration, milling and floating, heap and dump leaching, and magnetic separation are the beneficiation methods used. Gold, silver, and the platinum group elements are often processed by leaching the heaps with cyanides or by amalgamation. The amalgamation process using mercury is especially of high environmental concern because during this process, large quantities of mercury are required and released into the environment. This procedure is widely used in low- and middle-income countries in uncontrolled, small-scale mining operations (Limbong et al., 2003; Farrell et al., 2004; Kippenberg, 2011). For lead, zinc, and copper, milling, flotation, smelting, and leaching with sulfuric or hydrochloric acid are the methods used. Iron is principally extracted by magnetic separation. After extraction, waste rock residues, which may contain toxic extraction chemicals and heavy metals, are disposed of in tailings dams or abandoned as waste rock legacies posing environmental risk (United States Environmental Protection Agency, 1995; International Council on Mining & Metals, 2012). Common chemicals of environmental concern that are used for the processing and extraction of ores and minerals are: hydrochloric acids, sulfuric acid, potassium cyanide and cyanide acids, soda ash, sulfur dioxide, coal tar, and aluminum and zinc sulfates. The quantities of these chemicals used and their risks to human and environmental health are even harder to assess than those of the mineral and metals (United States Environmental Protection Agency, 1995). Even though these pollutants are of environmental concern, in this chapter we focus more on the most hazardous heavy metals, metalloids, and minerals that are released accidentally as side products and that pose risks to the environment.

Impact of ore refining

The pre-treated material is freighted to a smelter where impurities are removed under high temperature to produce the pure raw product, which can be traded and used. During the whole metal production cycle, the smelting of ores consumes the most energy and creates high levels of air pollutants, especially if the smelters or refineries are unregulated and if obsolete methods are used (Farrell et al. 2004; Blacksmith Institute and Green Cross, 2013).

During the processes involved in the exploitation, transport, extraction, and processing of metals and minerals, large amounts of hazardous heavy metals and minerals are unintentionally released into the environment. The minerals and metals of most concern are asbestos and antimony, arsenic, cadmium, chromium, copper, lead, manganese, mercury, and thallium. The products accumulate and remain in the soils next to the mining areas and at the mineral and mining processing facilities (Ayres, 1992; Stoeppler, 1992; Blacksmith Institute and Green Cross, 2012). In general, the accumulation and distribution of these compounds result from such processes as the leaching of heavy metals from tailings and by acid

Main Issues

The main issues associated with mining activities, which especially hold true for low- and middle-income countries, are that:

- Mining (especially open-pit mining) results in the destruction and deforestation of vulnerable natural environments (Farrell et al., 2004; Swenson et al., 2011).
- In mining processes, very large amounts of hazardous extraction chemicals or contaminated waste rocks are released and disposed of into the environment (Farrell et al., 2004; Liu et al., 2005) or abandoned in the mining sites. Acid drainage from the mines can also result (Naicker et al., 2003; Johnson and Hallberg, 2005; Lin et al., 2007; Tutu et al., 2008).
- In low- and middle-income countries particularly, the mine employees often work under poor and insecure conditions and they use obsolete and hazardous extraction methods. Often the legislative framework to manage these issues is missing or not well implemented (van Straaten, 2000; Limbong et al., 2003; Smith, 2011; Blacksmith Institute and Green Cross, 2012).

mine drainage (AMD). Alternatively, these compounds can be distributed as airborne particles and through adsorption onto aerosols as a result of the smelting and industrial processes.

Toxicological potential

In general, it is possible to distinguish between those trace elements that are essential for plant, animal, and human nutrition and those that are not. There are some elements that are required and beneficial for growing, enzymatic processes, and metabolism. A shortage of these essential elements would cause significant deficits in growth, development, metabolic activities, and, consequently, health. There are other elements for which plants, humans, and other animals have no demonstrated biological requirements, but for which exposure is associated with significant toxic effects. The highest concentration or dose of essential and non-essential metals that does not cause statistically significant adverse effects to the exposed population or biota is referred to as the 'no observed adverse effect level' (NOAEL). However, for both, essential and non-essential metals, a threshold can be reached where a further increase in concentration or dose does adversely affect the health of plants, animals, and humans and can even lead to death (see Figure 18; Goyer, 1997; Adriano, 2001). The lowest concentration level or dose that causes significant effects to living organisms is referred to as the 'low observed adverse effect level' (LOAEL).

Trace metals (and metalloids) such as cobalt, copper, iron, manganese, molybdenum, nickel, selenium, and zinc are essential to plants, humans, and other animals. In contrast, aluminum, antimony, arsenic, beryllium, bismuth, cadmium, gold, lead, mercury, platinum, silver, and tungsten are not essential for plants, humans, and other animals (Adriano, 2001; Luoma and Rainbow, 2008).

Furthermore, it is recognized that metals released into the environment pose one of the most serious pollution problems of today (Chandra Sekhar et al., 2003). This problem results from their specific characteristics. For example, they are non-biodegradable and non-thermo-degradable: heavy metal contamination can last for hundreds and even thousands of years if the contaminants are not physically or chemically immobilized or removed (Bohn et al., 1985; Mapanda et al., 2005). The half-live of cadmium in the soil is from 15 to 1100 years. That of copper is between 310 and 1500 years, while that of lead is between 740 and 5900 years. These wide variations in half-lives depend on the soil type and its physicochemical parameters (Alloway and Ayres, 1993). Consequently, heavy metal concentrations can increase unnoticed over time and reach hazardous or even toxic concentrations (Bohn et al., 1985). In the World's Worst Pollution Problems 2012 annual report, the Blacksmith Institute and Green Cross estimated that in low- and middle-income countries the health of about 14 million people is at risk as a result of mining and ore processing activities (Blacksmith Institute and Green Cross, 2012).

Metals released into the environment pose one of the most serious pollution problems of today as they are non-biodegradable and non-thermo-degradable and therefore can last for hundreds and even thousands of years if the contaminants are not physically or chemically immobilized or removed.

Generally, comprehensive data about most mining pollutants are not available and this is especially so in low- and middle-income countries. It is next to impossible to assess the consumption, occurrence, and fate of, and risks arising from the use of extraction chemicals such as cyanides (used for extracting precious metals) and sulfuric and hydrochloric acids (used for extracting lead, zinc and copper).

In this section about mining pollutants, the minerals and metals of highest environmental concern and for which the most comprehensive data are available were selected. Similar issues and trends hold true for other hazardous mining commodities, but they are not considered in this report. In this report, the selected pollutants

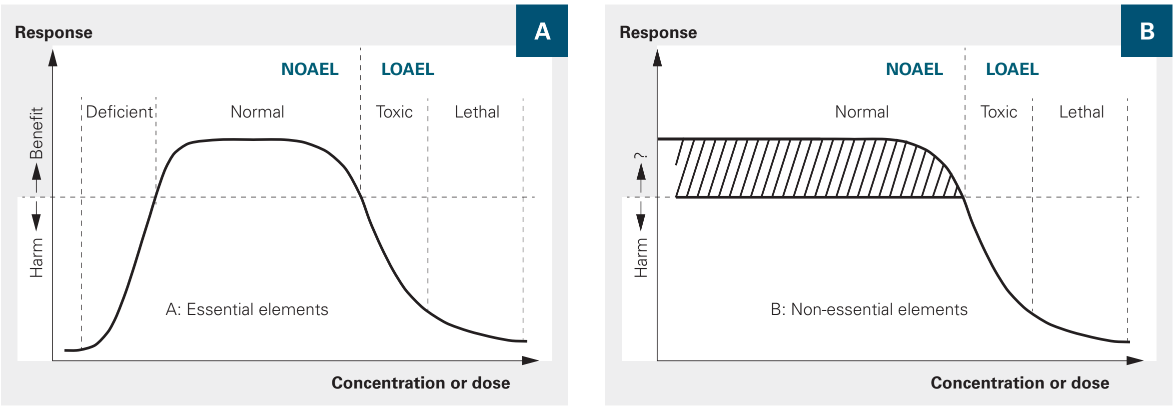

***Figure 18**: Dose-response relationship for essential (A) and non-essential (B) elements in plants, humans, and other animals (modified from Adriano, 2001)*

known for being of the highest environmental concern are (Ayres, 1992; Stoeppler, 1992; Blacksmith Institute and Green Cross, 2012):

- The metals (Group A). These include cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), and thallium (Tl)
- The metalloids (Group B). These include antimony (Sb) and arsenic (As)
- The minerals (Group C). This includes asbestos (ASB)

Considerable amounts of Cd are released into the environment as a by-product of mining production. This is especially the case in the exploitation of Zn and Pb ore fields.

Since the industrialization of the 19th century and the concomitant increase in mining activities, these metals and minerals have become relevant environmental pollutants. This is especially so for Cd, Cr, Cu, and Pb. Given their recent considerable global increases in production; they are of high environmental concern (Barrientos and Soria, 2013; United States Geological Survey, 2013)

Mining pollutants of environmental concern

Group A: Cadmium (Cd)

Introduction

Cadmium is a transition metal that is found mainly in minerals in combination with zinc (Zn), but also in ores together with Cu and Pb (Godt et al., 2006). The sulfide and carbonate minerals – spahlerite/wurzite, smithsonite, boulangerite, tetrahedrite, stannite, and chalcopyrite (in descending order of importance) – are the main ores of Cd with concentrations of the metal ranging from 15 to 50,000 ppm (Vlasov et al., 1966; Brehler et al., 1969; Schwartz, 2000). On average, the Earth's crust contains 0.11 – 0.5 ppm Cd (Fassett, 1975; Salomons and Förstner, 1984; Giuffré de López Camelo et al., 1997).

Cd is one of the metals of highest human and environmental concern, because of its relatively high water solubility, its mobility and its toxic effects even at very low concentrations.

Given its resistance to corrosion, the demand for cadmium has increased with a corresponding increase in primary production (Fassett, 1975). Generally, Cd is used in electroplating, pigments, plastic stabilizers, and nickel-cadmium batteries (Hutton, 1983). In 1910, the global production of cadmium was 50 tonne, and 17,000 tonne were produced in 1969 (Teworte, 1974). In 2012, world production of Cd stabilized at around 23,000 tonne (United States Geological Survey, 2013).

Considerable amounts of Cd are released into the environment as a byproduct of mining production. This is especially the case in the exploitation of Zn and Pb ore fields (Hutton, 1983; Sanità di Toppi and Gabbrielli, 1999; Benavides et al., 2005). Processes like AMD at orphan mining sites and the leaching of heavy metals into the groundwater and surrounding soils from abandoned waste rock heaps and tailings are further sources from which Cd or other hazardous metals enter into the environment (Farrell et al., 2004; Blacksmith Institute and Green Cross, 2011). The primary and secondary production processes of Cd and Zn, such as thermal smelting and electrolytic extraction, result in the emission of Cd aerosol particles. These precipitate in soils and surface waters near the production facilities, particularly if no aerosol filtering systems are used, obsolete techniques are applied, and insufficient controls are in place. This can be assumed to be the case in several regions in low- and middle-income countries (Díaz-Barriga et al., 1993; Razo et al., 2004). Additional Cd sources apart from mining are the burning of fossil fuels (mainly coal), emissions at power stations, heating systems, metal working industries, urban traffic, and cement and steel production. Contamination with Cd also occurs as a result of the emission or inappropriate disposal of solid wastes or waste incineration. Furthermore, phosphate rocks, used for the production of fertilizer, can contain traces of cadmium and these act as additional Cd sources into the environment (Bertine and Goldberg, 1971; Hutton and Symon, 1986; Jensen and Bro-Rasmussen, 1992; Sanità di Toppi and Gabbrielli, 1999; Godt et al., 2006).

Environmental behavior and occurrence

Cadmium has a relatively high water solubility (Fassett, 1975; Lockwood, 1976; Benavides et al., 2005). This depends on several factors. One of the main factors influencing the solubility in water is pH. At lower pHs, around and below 8, Cd becomes more soluble in water and occurs mainly as Cd^{2+} ions. At higher pHs, Cd has the affinity to precipitate as the predominant Cd salt, $CdCO_3$, or it forms complexes with other ligands. With increasing salinity, the predominant Cd species are chloro-complexes with $CdCl^{+}$ at lower salinities and $CdCl^{2}$ at higher salinities (Turner et al., 1981; Comans and van Dijk, 1988). Cd is one of the metals of highest human and environmental concern, because of its relatively high water solubility, its mobility and its toxic effects even at very low concentrations (Benavides et al., 2005).

The human uptake of Cd happens mainly through inhalation of Cd-bound airborne particles from burning processes, smoking, and from ingesting contaminated food and water (Godt et al., 2006).

Additionally, it has been shown that plants have an affinity to take up Cd at high rates and that it accumulates in the roots and shoots. This uptake and accumulation process is dependent on the type of soil, the pH, and the nutrient content of the soil. Soils, plants, and drinking water aquifers close to mining sites, smelters, and industrial districts can register higher levels of Cd or other hazardous metals (Benavides et al., 2005; Yang et al., 2006).

In high-income countries (HICs) like Australia, New Zealand, Denmark, Sweden, and the USA, natural mean concentrations ranging from 0.13 to 0.71 µg Cd/g have been measured in agricultural soils (McDowell et al., 2013). A mean dissolved Cd concentration of 0.02 µg/L was measured in two French rivers (Deycard et al., 2014).

In low- and middle-income countries, such as southern China, particularly in the Wu Jiand River basin where untreated mining wastewater is used for irrigation, high mean Cd concentrations of 13.59 µg/g dry weight in paddy soils and 8.21 µg/g dry weight in the roots of rice plants have been found (Yang et al., 2006). In this region, it is estimated that a 60 kg adult ingests about 132 µg of Cd per day. This exceeds the acceptable daily intake (ADI) of 70 µg of Cd (for an average adult weighing 70 kg). This figure of 70 µg/day is obtained from the provisional tolerable weekly intake (PTWI) of 7 µg/kg for a 70 kg adult (Food and Agriculture Organization and World Health Organization, 2003). In soils at mining sites in Zacatecas State, Mexico, elevated Cd concentrations of from 11 to 47 µg/g of air-dried soil were found (Carrillo González and González-Chávez, 2006).

Toxicity

As previously mentioned, the ADI of Cd is 70 µg. The US Environmental Protection Agency's low maximum contaminant level (MCL) is 5 µg Cd/L (Table 5). This is the level that should not be exceeded in drinking water to guarantee public health. These figures indicate the high toxicity of Cd (Food and Agriculture Organization and World Health Organization, 2003; United States Environmental Protection Agency, 2015c). Furthermore, Cd is not an essential element for plants, humans, and other animals (Adriano, 2001; Luoma and Rainbow, 2008). The uptake of Cd-oxides by inhaling tobacco smoke and breathing in occupational pollution causes acute respiratory distress syndromes and pulmonary edema. Long-term exposure leads to renal dysfunction, anemia, osteoporosis, and bone fractures (Friberg et al., 1985; Barbee Jr and Prince, 1999; Godt et al., 2006). In the human body, the kidney is the main target for bioaccumulation. There, the half-life of Cd is about 10 years (Orlowski and Piotrowski, 2003; Godt et al., 2006). In the kidney, chronic uptake leads to tubulus cell necrosis. The International Agency for Research on Cancer (IARC) classifies Cd as a Group I carcinogen for humans (International Agency for Research on Cancer, 1993). From mammalian in vitro experiments, there is evidence that exposure to cadmium salts promotes micronuclei and chromosomal aberrations and DNA strand breaks, and that the salts have a weakly mutagenic potential (Waalkes, 2003). In addition, although cadmium is not redox-active, there is evidence that exposure to Cd enhances the induction of oxidative stress (Shaikh et al., 1999; Ercal et al., 2001) and promotes the inhibition of several DNA-repair mechanisms (Hartwig and Schwerdtle, 2002). In short, Cd reacts with a wide variety of biomolecules, such as DNA, proteins, and membranes, with visible effects (Bertin and Averbeck, 2006). Given its toxicity, in Germany, the acceptable concentration of Cd in the blood of workers is not allowed to exceed 15 µg/L (Godt et al., 2006). In rat glioma cells an EC_{50} (24 hour) of 0.7 µmol/L of Cd has been identified.

Besides its toxic effects on mammals, Cd has negative effects on plant health and development.

Besides its toxic effects on mammals, Cd has negative effects on plant health and development. Among other adverse effects, it reduces the adsorption and transport of nitrates by inhibiting the nitrate reductase activity (Hernandez et al., 1996). It inhibits ATPase activity (Fodor et al., 1995), and disturbs chlorophyll biosynthesis (Stobart et al., 1985). The most visible symptoms of cadmium intoxication in plants are stunting leaf rolls and chlorosis (Das et al., 1997; Benavides et al., 2005).

From an environmental toxicological point of view, 24 hour EC_{50} values of between 180 µg/L *(Paramecium caudatum)* and 2650 µg/L *(Euplotes patella)* have been determined for these different ciliate species (Madoni et al., 1992). The reproduction of the water snail *Potamopyrgus antipodarum* was significantly affected at test concentrations of 25 µg Cd/L after exposure for 28 days (Sieratowicz et al., 2011). From an environmental toxicological point of view, even chronic concentrations of 0.08 to 0.25 µg/L of dissolved Cd can affect the health of aquatic organisms (Table 5; European Parliament and Council of the European Union, 2008).

Group A: Chromium (Cr)

Introduction

Chromium (Cr) is a transition metal and commercially mined as chromite ($FeCr_2O_4$). It occurs relatively frequently in nature. Hence, its average concentration in the Earth's crust is about 100 ppm (Salomons and Förstner, 1984; Barnhart, 1997).

Given its metallurgical properties Cr is used in alloys. For example, the addition of chromium during steel production helps to produce stainless steel which has corrosion and oxidation resistance characteristics. Furthermore, given its resistance to heat, it is used in refractory furnaces and foundry sands. In addition, Cr is used as a pigment for textile dyes, paints, inks, and plastics and in chemicals for leather tanning and preserving wood (Barnhart, 1997; Johnson et al., 2006; Straif et al., 2009; Blacksmith Institute and Green Cross, 2011). It is contained in the raw material used for cement production and as a trace element in phosphorus fertilizers. (Giuffré de López Camelo et al., 1997). Thus chromium has a wide range of applications, which explains why it is one of the most widely used metals (Barnhart, 1997). In 2012, worldwide mining production was about 24 million tonne (United States Geological Survey, 2013).

Chromium is in the waste rocks, slag, and solid wastes of mining processes and in the wastes of refineries and metal and e-waste recycling facilities.

Chromium is released into the environment during mining activities, its extraction and smelting, the burning of fossil fuels (especially coal), and industrial activities (steel production, metal alloy production, the textile industry, and tanneries). It is in the waste rocks, slag, and solid wastes of mining processes and in the wastes of refineries and metal and e-waste recycling facilities (Mukherjee, 1998; Johnson et al., 2006; Li et al., 2008c; Blacksmith Institute and Green Cross, 2011).

Environmental behavior and occurrence

Under environmental conditions, the most stable oxidation states of chromium are Cr(III) and Cr(VI). In aquatic systems, trivalent Cr is more likely to be precipitated as $Cr(OH)_3$, especially at pHs between 6 and 12. Outside these conditions, hexavalent Cr has a much higher water solubility and is, therefore, more transportable in water (Rai et al., 1989; Loyaux-Lawniczak et al., 2001). In the environment, Cr(III) is oxidized mainly by manganese oxides to the more hazardous Cr(VI). Hexavalent Cr is reduced to trivalent Cr by Fe(II), by mineral sulfides containing Fe(II), and by organic matter (Schroeder and Lee, 1975; Rai et al., 1989; Deng et al., 1996; Peterson et al., 1997; Loyaux-Lawniczak et al., 2001). In general, the hexavalent oxidation state of Cr is more stable in an oxidizing alkaline environment whereas trivalent Cr is more stable under reducing acidic conditions (Godgul and Sahu, 1995).

The natural levels of Cr in the surface soils of industrial countries, such as Denmark, Germany, Japan, USA, and Canada, range from 28 to 50 ppm dry weight (Kabata-Pendias and Pendias, 2001). In most of the drinking water sources in California, Cr(VI) concentrations ranged from 5 to 50 µg/L (Pacific Gas and Electric Company Groundwater Remediation Program, 2011).

Large amounts of heavy metals, such as Cr, continuously enter the environment from mining and industrial estates. The ambient air in western India contained chromium concentrations ranging from 0.016 to 0.089 µg Cr/m^3, and drinking water samples contained from 4 to 95 µg Cr/L (Sathawara et al., 2004). In a mining area in southern Togo, elevated levels of Cr between 182 and 1029 ppm were measured (Gnandi and Tobschall, 2002).

Toxicity

The chemical and biochemical reactivity, the toxicity, and the mobility of chromium as Cr(III) and as Cr(VI) are drastically different (Kotaś and Stasicka, 2000; Loyaux-Lawniczak et al., 2001). Cr(III) is an essential metal for animals and humans, but not for plants. For instance, it is crucial for the control of glucose and the lipid metabolism in mammals (Anderson, 1989). In contrast, Cr(VI) provokes several forms of cancer as a consequence of DNA damage and oxidative stress (Norseth, 1981; Gibb et al., 2000; Li et al., 2008c; Straif et al., 2009). According to the US EPA, the MCL of Cr in drinking water is 100 µg/L (Table 5) although Cr(III) is considered essential for animals and humans (Adriano, 2001). According to the IARC, hexavalent Cr is classified as a Group 1 carcinogen for humans (International Agency for Research on Cancer, 2012d). Between 1990 and 1993 in the EU alone, about 800,000 workers were estimated to have been exposed to Cr(VI) (Kauppinen et al., 2000). The Blacksmith Institute estimated that in their area of operation, 5.5 million people located in low- and middle-income countries are at risk from exposure to chromium alone (Blacksmith Institute and Green Cross, 2011). The main routes for hexavalent Cr uptake are through the inhalation of dust, mists, and fumes while working in the ore, metal, textile, and dye processing sectors. Cr(VI) is also absorbed through the skin. Smoking cigarettes is a significant source of Cr(VI) as well (Straif et al., 2009). Occupational exposure to Cr(VI) in the long term can lead to perforation of the nasal septum, asthma, bronchial inflammations, lung cancer, and inflammations of the larynx and liver. Skin contact results

The main routes for hexavalent Cr uptake are through the inhalation of dust, mists, and fumes while working in the ore, metal, textile, and dye processing sectors.

in allergies, dermatitis, dermal necrosis, and dermal corrosion (Lee et al., 1989; Straif et al., 2009; Bedi et al., 2013).

From an environmental toxicological perspective, the acute (96 hour) LC_{50} of hexavalent chromium of 41.75 mg/L for the freshwater fish *Channa punctatus* was investigated. Abnormal behavior, like erratic swimming and loss of equilibrium, and histopathological changes in gills and liver have been observed from exposure to 20 mg/L Cr(VI) (Mishra and Mohanty, 2008). Exposure to Cr(VI) causes adverse effects on plant growth and development. For higher plants, concentrations of about 100 µmol/kg dry weight of hexavalent Cr showed toxic effects (Davies Jr et al., 2002). For instance, Cr(VI) reduces the germination of seeds (Rout et al., 2000; Zeid, 2001). Hexavalent Cr hinders the uptake of nutrients and essential metals, such as nitrates, phosphorus, Fe, Mg, and potassium (Turner and Rust, 1971; Adriano, 2001). Additionally, it inhibits the growth of roots (Prasad et al., 2001), stems (Rout et al., 1997), and foliage (Sharma and Sharma, 1993). Furthermore, inhibition of photosynthesis and ATPase activity can be caused after exposure to Cr(VI) (Zaccheo et al., 1982; Vajpayee et al., 1999). For Cr(III) the chronic environmental quality standard (AA-EQS) is 4.7 µg/L and for Cr(VI) it is 3.4 µg/L (Table 5; UK Technical Advisory Group on the Water Framework Directive, 2008). Therefore, to guarantee the health of water organisms within an aquatic system, these concentrations should not be exceeded in the long term.

Group A: Copper (Cu)

Introduction

The transition metal copper (Cu) can be found as native copper and in the form of sulfides (chalcopyrite, bornite, and chalcocite), oxides (cuprit and tenovite), hydroxyl carbonates (malachite and azurite), and silicates (chrysocolla; Kruesi and Frahm, 1982). In the Earth's crust it occurs at an average concentration of 50–55 ppm (Taylor, 1964; Salomons and Förstner, 1984).

Copper has a wide range of uses. It has applications as a construction and building material, being used for water pipes, drain pipes, and plumbing fixtures primarily because of its light weight, its waterproofness, its flexibility, and its natural microbial resistance (Lehtola et al., 2004). Nowadays, plastic water pipes are frequently substituted for copper ones (United States Geological Survey, 2013). Because of the high electrical conductivity of copper even at low temperatures, it is used in the electronics industry in wires and electronic devices (Berman and MacDonald, 1952), and in transport equipment and vehicles (Berman and MacDonald, 1952; Kapur and Graedel, 2006). In addition, it is used as a pigment in ink and in the printing industry (Babler, 1998). It is used also in the metal industry to produce the alloys brass and bronze (Duke, 1944). Copper compounds are applied as wood preservatives (Hingston et al., 2001) and to purify water. Given its properties as an algaecide, fungicide, nematocide, and molluscicide, Cu is used as an antibacterial and antifouling agent (Fraser et al., 1974; Cooney and Tang, 1999; Borkow and Gabbay, 2005; Gabbay et al., 2006). Globally, annual copper production has increased immensely. In 1968, 5.8 million tonne (Förstner and Wittmann, 1979) of Cu was produced, increasing to 8.3 million tonne in 1985 (Bowen, 1985). By 2012, world mining production of copper reached 17 million tonne (United States Geological Survey, 2013).

Copper is introduced into the environment in a large number of ways. Mining and metal processing activities, such as smelters and refineries, brass mills, and bronze production are some such sources. Other sources include the cement industry, its use as an aquatic pesticide against fungi, bacteria, and algae (McKnight et al., 1983; Richardson, 1997), and the disposals of e-waste and construction materials (Flemming and Trevors, 1989).

Environmental behavior and occurrence

Cu has three oxidation states, Cu(0), Cu(I), and Cu(II) (Flemming and Trevors, 1989). At pH values up to 6, Cu(II) occurs in aquatic systems as dissolved Cu^{2+} ions. With increasing pH, Cu(II) species, such as $Cu_2(OH)_2^{2+}$, $CuOH^+$, and $CuCO_3$ are predominant (Sillén and Martell, 1964; Sylva, 1976; Luoma and Rainbow, 2008). Cu(II) is a potent complexing agent and in the positive charged form it has a high tendency towards hydrolysis (Flemming and Trevors, 1989). The Cu levels in solution are regulated by different processes: complexation to inorganic (more predominant in seawater than in freshwater; Leckie and Davis, 1979; Flemming and Trevors, 1989) or organic ligands (in fresh and seawater), precipitation as oxides, hydroxyl carbonates, silicates, and sulfide minerals (Sylva, 1976; Elder and Horne, 1978; Kruesi and Frahm, 1982; Davis, 1984; Coale and Bruland, 1988), and adsorption to biota and organic particles (Ramamoorthy and Kushner, 1975; Ramamoorthy and Rust, 1978; Kuo and Baker, 1980). These processes control the presence of the different Cu species, increase or decrease their mobility within aquifers, and affect their availability, uptake, and further adsorption to biota (Flemming and Trevors, 1989). Because of these interactions, Cu is distributed among three different phases – the aqueous phase (as free ionic and water soluble complexes; Sylva, 1976), the solid phase (as particles, colloids, soils and sediments), and the biological phase (adsorbed and absorbed in biota; Flemming and Trevors, 1989; Luoma and Rainbow, 2008).

Natural Cu concentrations in freshwater range from 0.03 to 5 µg/L (Hodson et al., 1979; Bowen, 1985; Luoma and Rainbow, 2008). In uncontaminated soils, Cu concentrations between 16 and 25 µg/g have been found (Hornberger et al., 2000).

An example of environmental pollution occurs in northern Chile, near the city Chañaral. Here, extensive copper mining had been conducted for more than 60 years. Untreated tailings water was disposed of directly into the sea causing drastic beach degradation and a decrease in biodiversity with a loss of invertebrates and algal species (Castilla, 1996; Medina et al., 2005). Years after this exposure, elevated Cu concentrations of between 34 and 50 µg/L could be measured in the water samples of this coastal region (Castilla, 1996; Medina et al., 2005). Elevated Cu concentrations of between 12 and 43 µg/g were measured in sediments of the River Yamuna in India (Jain, 2004). This contamination is more related to the activities of the textile and printing industries and to the disposal of city waste than to the mining industry (Jain, 2004).

Toxicity

Although Cu is essential for several organisms, low concentrations of Cu can have harmful effects on the ecosystem by affecting bacteria, algae, fungi, plants, fish, and invertebrates, particularly in aquatic systems.

The toxicity of Cu is relatively low for mammals and humans because the MCL of Cu in drinking water is 1.3 mg/L. The MCL of the more toxic cadmium is much lower at 5 µg/L (Table 5; United States Environmental Protection Agency, 2015c). Although copper is an essential human nutrient, concentrations above the MCL cause gastrointestinal upsets such as diarrhea, abdominal cramps, and nausea, especially in children. These symptoms are less life-threatening than those of previously mentioned metals (Knobeloch et al., 1994). As there is no evidence that Cu can promote the formation of cancer, it is not classified by the IARC as carcinogenic to humans. Concentrations of 50 to 250 mg/kg copper sulfate are used as a food additive in the diet of pigs to promote growth. These animals can tolerate quite high levels of Cu in their diets (López Alonso et al., 2000). In addition, Cu is essential for plants and for that reason it is added to several fertilizers (Adriano, 2001; Xiaorong et al., 2007).

The environmental toxicological perspective is different. Even though Cu is essential for several organisms, low concentrations of Cu can have harmful effects on the ecosystem by affecting bacteria, algae, fungi, plants, fish, and invertebrates, particularly in aquatic systems (Castilla, 1996; Erickson et al., 1996; Santore et al., 2001; Li et al., 2008b; Rofkar et al., 2014). Several investigations and the reviews of Flemming and Trevors have shown that cupric copper (Cu^{2+}) in particular, and the $CuOH^{+}$ and $[Cu_2(OH)_2]^{2+}$ complex ions are toxic Cu species (Pagenkopf, 1983; Flemming and Trevors, 1989; United States Environmental Protection Agency, 2008). They can interact negatively with essential proteins, enzymes, and nucleic acids at the cell wall, cell membrane, and within such microorganisms as algae, fungi, and bacteria. In addition, exposure to Cu can affect the regeneration of essential inorganic nutrients, inhibit growth and cell division, and inhibit photosynthesis, particularly for algae, cyanobacteria, and aquatic plants. This can have devastating effects on aquatic ecosystems since microorganisms are important primary decomposers of hazardous compounds that are hostile to life. These microorganisms are important also for their ability to regenerate inorganic nutrients; they are necessary primary producers of essential nutrients and oxygen (McBrien and Hassall, 1967; Swift et al., 1979; Kobayashi and Rittmann, 1982; Stauber and Florence, 1987; Flemming and Trevors, 1989; Chaudhry and Chapalamadugu, 1991; Rofkar et al., 2014). Even a single exposure to 10 µg Cu/L leads to a significant, though reversible, reduction in algal biomass and chlorophyll, with negative consequences for photosynthesis. These impacts were not reversible at a test concentration of 40 µg Cu/L (Elder and Horne, 1978; Flemming and Trevors, 1989). Furthermore, a $Cu(SO)_4$ concentration of 10 µg/L results in a significant decrease in the number of viable bacteria (Effler et al., 1980). The amphipod *Hyalella azteca* showed a LC_{50} of 31 µg/L (Ankley et al., 1993). In addition, for juvenile salmon weighing between 200 mg and 340 mg, the LC_{50} values (24 hour) for concentrations ranging from 3.59 to 29.9 µg/L were investigated. Comparable LC_{50} values (24 hours) from 22.8 to 115.7 µg/L were determined for juvenile rainbow trout weighing 600 mg (Buhl and Hamilton, 1990). In addition, a fish toxicity test was conducted with juvenile white sturgeon at two life stages, 8 days post hatch and 40 days post hatch. The median LC_{50} values ranged from 9 to 25 µg Cu/L (Vardy et al., 2014). These LC_{50} values emphasize that fish are highly susceptible to Cu. In fish and other aquatic vertebrates, copper binds to the gill membranes and can cause damage to and interfere with osmoregulatory processes (United States Environmental Protection Agency, 2008). From an environmental toxicological point of view, a chronic environmental quality standard (AA-EQS) of 1µg Cu/L is recommended (Table 5; UK Technical UK Technical Advisory Group on the Water Framework Directive, 2012).

Group A: Lead (Pb)

Introduction

The main host mineral of lead is galena (PbS), which contains about 86.6% lead. Other relevant minerals containing lead are cerussite ($PbCO_3$) and anglesite ($PbSO_4$) (Shukla and Leland, 1973). Often, Pb is found in ores together with Ag (silver), Zn, and Cu (Commonwealth of Australia, 2015). The average concentration of Pb in the Earth's crust ranges from 13 to 26 ppm. Although this amount is relatively low, Pb is not considered to be a rare element because it is easily extracted from ore and easily refined (Zimdahl et al., 1973; Salomons and Förstner, 1984; World Health Organization, 2011; Thomas Jefferson National Accelerator Facility, 2014).

With its high density, malleability, resistance to corrosion (though it does tarnish when exposed to air), low melting point, ease of fabrication, resistance to acid, and its photovoltaic activities, Pb has a wide variety of applications. In ancient times, it was used for making water pipelines, as a building material, and in glazes on ceramics. It was used for color pigments in paints and cosmetics, for armor, and as weights for fishing nets (Commonwealth of Australia, 2015; United States Geological Survey, 2011). Nowadays, Pb is used mostly in lead–acid batteries for vehicles and in industrial-type batteries (Bode, 1977; World Health Organization, 2011; United States Geological Survey, 2013; Commonwealth of Australia, 2015). In addition, Pb and Pb compounds are used for ammunition, to cover cables, in alloys, as additives in bronze and brass production, in the glass and ceramic industry, and in the construction material in the form of sheet lead. Furthermore, it is a shield for x-rays and is used as a noise control material. Lead compounds are employed as coatings for the paper used in photothermography, as stabilizers in plastic, and as vulcanizing agents in rubber and plastics. A few centuries ago it was used in paints and in plumbing material; now less toxic substitutes are used (Agency for Toxic Substances and Disease Registry, 2007b; National Toxicology Program, 2014b; World Health Organization, 2011). Organic lead compounds, like tetramethyllead and tetraethyllead, were used extensively in gasoline as anti-knocking agents from 1992 until the end of the 19th century, when the user of organic Pb compounds was banned. The addition of organic Pb compounds to gasoline resulted in a significant global increase in Pb emissions from car exhaust fumes into the environment (Nriagu, 1990b; von Storch et al., 2003). In low- and middle-income countries, especially in Africa, the enforcement of the ban on organic lead compounds as an anti-knocking agent was delayed. However now, the use of lead compounds in gasoline has been reduced worldwide (United Nations Environment Programme, 1998b; Phiri, 2006). To meet the constantly growing demand for Pb, 5.2 million tonne of Pb were extracted by mining in 2012. Compared to 2011, the production of lead worldwide increased by nearly 10% (United States Geological Survey, 2013).

Today, the main entry pathways for lead into the environment are waste effluents and aerosols that are released into the environment from lead recycling processes, from lead-acid batteries, and the recycling of other e-waste and scrap. Smelters, foundries, and other industrial processes, such as the production of plastic and rubber, the burning of coal (Tang et al., 2008), weapon and ammunition production, and ceramic and glass manufacturing, can emit high amounts of Pb into the environment as well. This is especially the case if no appropriate filter systems are used during the heating and smelting processes. Other significant sources of Pb are mining activities and the extraction of Pb, Ag, Zn, and Cu ores (Agency for Toxic Substances and Disease Registry, 2007b).

Environmental behavior and occurrence

Pb occurs rarely in its elemental state, Pb(0). It is more likely to be present in its bivalent form, Pb(II) (Agency for Toxic Substances and Disease Registry, 2007b). In general, lead accumulates in plants, algae, invertebrates, and vertebrates (Bowen, 1966; Cox and Rains, 1972; Spehar et al., 1978; Freeman et al., 1992; Namihira et al., 1993; Adriano, 2001; Luoma and Rainbow, 2008). The distribution of lead and other metals and transition metals in the matrices of the environment and its uptake by biota depend on several factors. These include pH, redox potential, concentration of chelating agents, soil composition, chemical composition of the metallic compound, and the hardness of the water (Adriano, 2001). In general, low pH and low redox potential increase the mobility of Pb in water, and its solubility depends on the chemical composition as well (Adriano, 2001). In soils with low pH (from 3 to 5), PbO showed the highest solubility in water; $PbCO_3$ and $PbSO_4$ are less soluble (in descending order of solubility). At pH 7, $PbSO_4$ is the most soluble Pb compound and PbO and $PbCO_3$ become less water soluble (in descending order of solubility; Cao et al., 2008). This solubility promotes the leaching of Pb from tailings and soils. Acid mine drainage contributes as well (Vymazal, 1990). Lead compounds, such as lead acetate, lead nitrate, and lead chloride are soluble or miscible with water. Lead arsenate, lead acids, halogenated lead compounds, lead thiocyanates, lead phosphates, and lead sulfates are Pb compounds with lower solubilities (National Toxicology Program 2014b).

The natural level of lead in freshwater is 3 µg/L and in freshwater sediments it is 40 µg/g. Soils have a background content of about 10 ppm (Vymazal, 1990).

Elevated Pb concentrations of environmental concern, ranging from 71 to 2190 ppm in dry stream sediments have been found at the recent mining site of Villa de la Paz-Matehuala, Mexico (Razo et al., 2004). Lin et al. (2007) investigated the chemical dynamics and environmental toxicity of a river, located in a tributary basin area of the Pearl River in China, affected by AMD. In this instance, the AMD was induced by a flood event which occurs periodically every 100 years. In floodwater samples near the Dabaoshan mine, Pb concentrations of between 0.7 and 7.2 mg/L were measured 3.5 km from the point source. Elevated Pb concentrations up to 0.2 mg/L were measured 16 km from the point source (Lin et al., 2007). In soil samples at the Chenzhou lead/zinc mine, Pb concentrations of up to 1061.54 mg/kg were measured (Liu et al., 2005). In this region, the Pb concentrations were 1.91 ppm in maize, 4.58 ppm in capsicum, and 9.00 ppm in taro. Elevated Pb concentrations of 1.399 mg/L were measured in the Pilcomayo River in Argentina and levels of 2.201 mg/L were found in the Tarapaya River in Bolivia. This contamination originates from the extensive mining in these areas (International Agency for Research on Cancer, 2006b). The results show that although most of the studies about the consequences of AMD and the distribution of heavy metals from tailings were conducted in higher-income countries (USA, Canada, and Europe), considerable concentrations of hazardous compounds and metals from mining are found in low- and middle-income countries as well. This is especially the case where obsolete techniques are used for ore extraction and metal processing and if wastes, tailings, and the closing of mines are poorly managed.

Chronic exposure to higher concentrations of Pb, mainly from occupational exposure or living close to smelters, metal processing and recycling industries, lead–acid battery manufactories, and mining areas, may result in an accumulation of Pb in the liver, lungs, spleen, kidneys, bone marrow, bones, teeth, and even the brain.

Toxicity

Occupational exposure, and the exposure of humans and other animals, to industrial estates and metalworking industries, lead or other metals, remain a seriously disputed issue. This is particularly so in low- and middle-income countries and even in HICs (Staudinger and Roth, 1998; Tong et al., 2000). The IARC lists inorganic Pb compounds in Group 2A as probable human carcinogens. Organic lead compounds were classified in Group 3 as not being carcinogenic to humans (International Agency for Research on Cancer, 2006b). This categorization shows that inorganic Pb compounds have a higher toxicity than organic ones. According to the US EPA, the MCL for drinking water is about 0.015 mg/L (Table 5). The low value of this limit indicates that an exposure to lead compounds in the long term has adverse effects on human health. Children and pregnant women seem to be most susceptible (United States Environmental Protection Agency, 2015c; World Health Organization, 2011). Also, Pb is not beneficial to plants, animals, and humans (Adriano, 2001). Pb can enter the blood stream from the alveoli by inhaling lead dust or fumes and it can enter the intestine by ingesting contaminated food and water. Lead is discharged from the body in urine and feces (Agency for Toxic Substances and Disease Registry, 2007b; World Health Organization, 2011). The circulation of the blood distributes the Pb throughout the whole body (Ong and Lee, 1980; World Health Organization, 2011). Chronic exposure to higher concentrations of Pb, mainly from occupational exposure or living close to smelters, metal processing and recycling industries, lead–acid battery manufactories, and mining areas, may result in an accumulation of Pb in the liver, lungs, spleen, kidneys, bone marrow, bones, teeth, and even the brain (Agency for Toxic Substances and Disease Registry, 2007b). According to several investigations, Pb is suspected to cause the formation of several forms of cancer, especially in the lungs, kidney, and brain, though there are converse results as well (Steenland and Boffetta, 2000; World Health Organization, 2011). Hartwig (1994) showed there is evidence that exposure to Pb in vitro can enhance the mutagenicity of other mutagens by inhibiting the repair of DNA. In addition, increased chromosome aberrations or sister chromatid exchanges were found in exposed workers (Mäki-Paakkanen et al., 1981). Lead has adverse neurological effects on humans and other mammals. Significant behavioral and cognitive deficits, such as malfunctions in activity, adaptability, attention, reduced memory and learning ability, up to irreparable mental retardation, are observed after continuous exposure to Pb (Horn Rummo et al., 1979; Gilbert and Rice, 1987; Schwartz and Otto, 1987). WHO recommends not exceeding an ADI of 250 µg for a 70 kg adult. Globally, the limit for drinking water should not exceed 10 µg/L and that for air should not exceed 0.5 µg/m^3 (World Health Organization, 2010a). Keeping the level of lead in the blood below between 10 and 20 µg/100 ml would prevent lead poisoning or problems in neuropsychological development, especially for children (United Nations Environment Programme, 1998a; Gidlow, 2004).

From an environmental toxicological point of view, Pb affects the health of vertebrates and primary producers as well. For instance, rainbow trout were significantly affected after exposure to dissolved lead. In toxicity tests in hard and soft water, they showed an LC_{50} (96 hour) ranging from 1.17 to 1.47 mg/L. In addition, chronic exposure (6–7 month) to 0.064 mg/L Pb enhanced the formation of physical abnormalities in fingerling rainbow trout (83 mm length). At this concentration, the tail of the tested rainbow trout turned black. A month later, the trout exhibited spinal curvature as a result of dorsal-ventral spinal flexures (lordosis), and/or bi-lateral spinal flexures, described as scoliosis and degeneration of the caudal fin. The formation of these abnormalities can be explained as direct or indirect influences on the central nervous system or biochemical inhibition in the metabolism (Davies et al., 1976).

Plants are capable of taking up and accumulating Pb as well (Deng et al., 2004; Rotkittikhun et al., 2006). In general, the roots are able to accumulate the most Pb, followed by the leaves, stem, inflorescence, and seeds, in descending order. This order can differ between individual plant species (Antosiewicz, 1992). Lead uptake can lead to several adverse effects, such as inhibition of enzymatic activities and photosynthesis, disturbance of the uptake of essential minerals and nutrients, and impairment of membrane permeability. These problems lead to inhibition of root growth, stunted growth of the plant in general, and even chlorosis (Burton et al., 1984; Sharma and Dubey, 2005). For instance, after a 20 day exposure of rice seedlings to 103.6 and 207.2 mg $Pb(NO_3)_2$/L, root growth was inhibited by 22 to 42% and shoot growth was reduced by 25% compared to a control without exposure to Pb (Verma and Dubey, 2003). For the algae (diatom) *Phaeodactylum tricornutum*, short-term exposure to 7.5 mg Pb/L caused complete inhibition of photosynthesis (Woolery and Lewin, 1976). The chlorophyte *Chlamydomonas reinhardii* seemed to be more resistant to exposure to Pb, showing a 47% reduction in growth after exposure for 48 hours to 0.207 mg Pb/L (Irmer, 1985). According to the estimated chronic environmental quality standard, a concentration above 0.0012 mg/L (Table 5) in the long term can impair the health of aquatic organisms (European Parliament and Council of the European Union, 2013).

The uptake of lead can have several adverse effects for plants, leading to inhibition of root growth, stunted growth of the plant in general, and even chlorosis.

Group A: Manganese (Mn)

Introduction

Manganese appears as a whitish-grey metal, mainly in coexistence with iron (Fe). Because of that, they are similar in their chemical behaviors. It has a melting point around 1255°C and it oxidizes in air and rusts under humid conditions. While it is harder than Fe, it is relatively brittle. Principally, it is deposited as manganese nodules on the ocean floor and the floors of freshwater lakes (Post, 1999). It is distributed and deposited in metamorphic, sedimentary, and igneous rocks in tropical, subtropical, and the warmer temperate zones of the Earth (Post, 1999). The main minerals of manganese are oxides, carbonates, and silicates – pyrolusite (MnO_2), rhodochrosite ($MnCO_3$), magnetite (MnO_3 * H_2O), hausmannite (Mn_3O_4), braunite ($3Mn_2O_3$ * $MnSiO_3$), and rhodonite ($MnSiO_3$). Manganese minerals are well distributed around the globe and occur frequently, with an average concentration in the Earth's crust of 1000 ppm (Salomons and Förstner, 1984; Adriano, 2001).

Manganese is used mainly as an additive during steel production. As an alloy, together with metals like chromium, aluminum, and zinc, it acts as an anti-corrosive agent during the production of stainless steel and provides strength, toughness, and hardness (Adriano, 2001; International Manganese Institute, 2014). Given its metallurgical properties, it is used in the production of several alloys of steel, aluminum, and copper. Additionally, Mn is used for non-metallurgical purposes as well. For instance, it is used in the production of alkaline batteries, electronic coils, matches and fireworks, welding rods, as a dye in paints, and in the ceramic or glass industry (as a decolorizer or as a pigment). Furthermore, Mn compounds are found in paints, varnishes, and oils as drying agents. They are used as disinfectants, animal food additives, and as bleaching agents in the textile industry and in the tanning of leather. Manganese oxides and Mn chlorides are used in dry cell batteries and as catalysts. Organic Mn compounds (methylcyclopentadienyl manganese tricarbonyl – MMT) are used as an anti-knock agent in fuels as substitutes for methylated Pb compounds, as fungicides (e.g. maneb and mancozeb), and they are contained in contrast agents used in resonance imaging (Adriano, 2001; Santamaria, 2008; United States Geological Survey, 2013). Manganese is the fourth most widely used metal in the world. For instance in 2011, worldwide production of manganese alloys was 17.7 million tonne (International Manganese Institute, 2014).

Manganese is mainly released into the environment from mining activities, manufacturing and metal processing activities, and as an anti-knock agent in fossil fuels. Its toxicity is less pronounced than that of other metals like Pb, Cd, Hg, and Cr (Santamaria, 2008).

Environmental behavior and occurrence

Overexposure to Mn can have an adverse effect on humans and can affect the health of other animals. Once Mn has passed through the blood–brain barrier, it causes neurodegenerative impairment resulting in syndromes comparable to those of idiopathic Parkinson's disease.

Manganese can be found in oxidation states I, II, III, IV, VI, VII. Generally, in nature, salts with the oxidation states II, IV, VI, and VII are the most stable. MnO, $MnCO_3$, and Mn_2O_3, with lower atomicity (II-III), are alkaline and Mn compounds with higher oxidation states are acidic (Adriano, 2001). The oxidized form Mn(II) is very stable in an acidic milieu and MnO_2 is more stable under basic conditions in the presence of oxygen. Divalent Mn is less likely to form complexes with other ligands, whereas Mn(III) can form complexes with phosphorus compounds and with other organic compounds (Adriano, 2001; Santos-Burgoa et al., 2001; Yakushev et al., 2009).

In general, the biogeochemistry of Mn is quite complex, mainly because of its occurrence in several oxidation states and because Mn oxides can occur in crystalline or pseudocrystalline forms. In addition, the oxides are often coexistent with Fe oxides. Iron and Mn hydroxides show amphoteric characteristics, which means that they can act as a base or as an acid by having the tendency to react with both cations and anions. Microbiological activities and physical and chemical factors control the oxidation-reduction reactions of Mn compounds. For plants, the uptake of Mn(II), organic Mn compounds, Mn oxides, and soluble Mn silicates seems to be of highest relevance. Especially at lower pH values, lower redox potentials, and under reducing (anaerobic) conditions, Mn is more soluble and more available for uptake via roots (Boxma and De Groot, 1985; Brookins, 1988; Patrick and Jugsujinda, 1992; Adriano, 2001).

Mn occurs naturally in soils at levels around 1000 ppm (Salomons and Förstner, 1984; Adriano, 2001). However, elevated Mn contamination can be found in water or soil samples in low- and middle-income countries in areas with high levels of mining activity. For instance, investigations in a Mn mining district in central Mexico showed elevated environmental mean concentrations of 45.34 mg Mn/L (maximum, 240.25 mg Mn/L) in river water samples, 119.25 mg Mn/kg (maximum, 264.00 mg Mn/kg) in soil samples, 39.95 mg Mn/L (maximum, 241.90 mg Mn/L) in well water, and 20.2 mg Mn/ dry kg (maximum, 52.5 mg Mn/ dry kg) in ready to eat food (Santos-Burgoa et al., 2001). In the Lipu manganese mine area in Guangxi, South China, elevated environmental concentrations of Mn and other heavy metals were found as well. There, in an area of bare mining land with tailings, soil concentrations up to 10,000 mg Mn/kg (ppm) were reached. An adjacent region showed elevated concentrations up to 7600 mg Mn/kg (ppm). In an adjacent restored mining area with an artificial chestnut forest and a dense shrub belt, elevated Mn concentrations of around 2000 ppm were measured. In addition, the results indicate that plants are embedding considerable amounts of Mn, particularly in their roots and leaves. In 12 dominant species in the Lipu Mn mine district, concentrations of 17.4 to 816.5 mg Mn/kg (ppm) were found in the roots and levels of from 89.2 to 3280.0 mg Mn/kg (ppm) were measured in the leaves (Li et al., 2007).

Toxicity

For human beings and other animals, the uptake of Mn is essential to guarantee normal development and body function (Keen et al., 2000). Mn binds to enzymes and controls enzymatic reactions. For instance, Mn acts as a fundamental co-factor for arginase, which enables urea production in the liver, and it is involved in enzymatic processes that reduce cellular oxidative stress (Carl et al., 1993; Keen et al., 2000; Crossgrove and Zheng, 2004). However, overexposure to Mn can have an adverse effect on humans and can affect the health of other animals. Once Mn has passed through the blood–brain barrier, it causes neurodegenerative impairment resulting in syndromes comparable to those of idiopathic Parkinson's disease (IPD; Barbeau, 1984; Cowan et al., 2009). Besides these impairments to the central nervous system, there is evidence from human and animal studies that overexposure to Mn can lead to interference with the function of the lungs, cardiac system, and liver. In addition, it can cause impairments to reproduction by decreasing fertility, increasing the formation of fetal abnormalities, and inhibiting fetal development (Crossgrove and Zheng, 2004). The main clinical symptoms of an overexposure to Mn are headaches and insomnia (86%), exaggerated tendon reflexes (83%), memory loss (75%), hyper-myotonia (75%), emotional instability (35%), hand tremor (23%), speech disturbances (6%), and festinating gait (3%; Crossgrove and Zheng, 2004).

The uptake of Mn occurs mainly through inhalation at ore exploiting areas, steel production, smelting, and battery manufacturing sites, or by ingesting contaminated food or water (Santamaria, 2008). Given its toxicity, WHO recommends a limiting value of 0.4 mg Mn/L for drinking water and has set the tolerable daily intake (TDI) at 0.06 mg Mn/kg of body weight. It should be noted that workers have shown significant clinical effects of Mn toxicity following continuous exposure to Mn concentrations higher than 5 mg/m^3 (Whitlock Jr et al., 1966; Cook et al., 1974; World Health Organization, 2004; Santamaria, 2008).

In plants, manganese is an essential micronutrient that is required for several functions. Plant respiration and the metabolizing of organic acids, P, and N depend on the availability of Mn. Furthermore, Mn is involved in the photosynthetic formation of oxygen in chloroplast (Römheld and Marschner, 1991). It is involved in protein synthesis, the control of the carboxylic acid cycle, and the metabolizing of carbohydrates (Adriano, 2001). Although Mn is essential for plants, human beings, and other ani- mals, it is one of the major factors limiting crop production, particularly on acidic soils. About 30% of the crops on the world's total land area are affected by Mn toxicity (Kochian, 2000; Alam et al., 2006). Furthermore, it has been shown that concentrations in plant tissues of from 100 to 500 mg/kg dry weight are enough to cause toxic effects (Jones, 1991; Adriano, 2001). As a consequence of overexposure of Mn, plants exhibit such symptoms as chlorosis, necrosis of leaves, leaf rolling, and inhibited plant growth. From the environmental toxicological point of view, the estimated AA-EQS of Mn was 0.123mg/L (Table 5; UK Technical Advisory Group on the Water Framework Directive, 2012). Therefore, although Mn is essential for all living organisms and it is not considered in many toxicological assessments (for instance, there is no US EPA MCL value for Mn), overexposure can cause significant toxic affects to plants, mammals, and humans.

About 30% of the crops on the world's total land area are affected by Mn toxicity.

Group A: Mercury (Hg)

Introduction

Elemental Hg appears as a silvery white metal and it is the only metal which is liquid at room temperature (Morel et al., 1998). In mining, the sulfide cinnabar (86.2% Hg) is most relevant, and other minerals, like metacinnabar and livingstone are less important exploitation sources for Hg. The average concentration of this transition metal in the Earth's crust ranges from 50 to 80 ppb (Fleischer, 1970; Salomons and Förstner, 1984; Adriano, 2001; Dong et al., 2013).

Mercury is used in many fields. Today, it is used primarily to extract gold and silver using the amalgam process during artisanal and small-scale mining operations (Farrell et al., 2004; Artisanal Gold Council 2015). The Artisanal Gold Council determined that 1620 tonne of Hg were used in artisanal gold mining in 2010 (Artisanal Gold Council 2015). In addition, it is used in high volumes as a catalyst during vinyl chloride monomer production and in the production of chlorine and sodium hydroxide using the chlorine-alkali process. Nowadays, especially in HICs, the more modern diaphragm and membrane method substitutes for the chlorine-alkali process (Pacyna et al., 2006; Swain et al., 2007). Mercury is used in the pulp and paper industry as a slimicide. Furthermore, old fluorescent lamps, batteries, dental amalgam fillings, paints, cosmetic products, antifungal agents for preserving wood, and pesticides can contain mercury. In HICs, the use of mercury has been reduced by finding alternative and equivalent substitutes. For instance, instead of amalgam, plastic and ceramic inlays now are used in dentistry. Fluorescent lamps containing Hg have been replaced by light-emitting diodes using indium or lithium. Nickel–cadmium and zinc–air batteries are substitutes for mercury–zinc ones. Digital thermometers or ones containing new alloys (galistan) are replacing ones containing mercury (United States Geological Survey, 2013). Medical and electronic devices and specific parts of cars (car switches) can contain small quantities of mercury (de Lacerda and Salomons, 1998; Adriano, 2001; United States Geological Survey, 2013). Although the use of mercury has decreased in HICs, it can be assumed that large amounts of mercury are still used in low- and middle-income countries. It has been shown that mercury has a net flow from higher-income to lower-income countries, because in the latter its use in the industrial and the mining sector is less constrained. Also it can be contained in electronic waste which is disposed of inappropriately in low- and middle-income countries (Maxson, 2005; Swain et al., 2007; International Labour Organization, 2012). To meet demand, 1600 tonne of mercury were mined in 2012, while additional mercury is produced from secondary recycling processes (United States Geological Survey, 2013).

Altogether, the highest global anthropogenic release of mercury into the environment is about 1960 t/year. This comes from artisanal gold mining (727 t/year), coal and oil combustion (483.9 t/year), non-ferrous metal production (193 t/year), cement production (173 t/year), large-scale gold production (97.3 t/year), waste disposal (95.6 t/year), emissions from contaminated sites (82.5 t/year), ferrous metal production (45.5 t/year), caustic soda production through chlorine-alkali processes (28.4 t/year), oil refining (16 t/year), and mercury mining production (11.7 t/year; United Nations Environment Programme, 2013a)

Environmental behavior and occurrence

Mercury is an omnipresent environmental pollutant of high concern, having natural and anthropogenic sources.

Mercury is an omnipresent environmental pollutant of high concern.

In the environment, Hg has three different oxidation states. It occurs as elementary Hg(0), as oxidized Hg(I) (mercurous Hg), and as Hg(II) (mercuric Hg; Adriano, 2001). Mercury is remarkable in that it can evaporate directly from water into the atmosphere, mainly as Hg(0). It can sublimate directly from solids and it occurs as inorganic salts, organic complexes, and as methylated compounds.

About 5000 t/year are stored annually in the atmosphere. The land stores about 1 million tonne and about 2.88 million t/year are deposited in the oceans (Swain et al., 2007). Given its physicochemical properties, such as its vapor pressure of 0.163 Pa at 20°C, its low melting point of -38.8 °C, and its water solubility of 60 µg/L (25°C), mercury has little tendency to dissolve in water and it is more likely to evaporate as elemental Hg or to be deposited in sediments, adsorbed to organic particles or absorbed by biota (Morel et al., 1998; Adriano, 2001).

There is evidence that Hg, particularly in the form of methylated Hg compounds, is accumulating among the food chain through biomagnification.

The partition of Hg among the different environmental compartments is quite complex and there are still some gaps in the knowledge. Elemental Hg (Hg(0)) evaporates from water and sediments and it is released into the air mainly from anthropogenic processes, such as artisanal gold mining and the combustion of fossil fuels. Mercury has a residence time in the atmosphere of about 1 year and it is distributed globally. In the atmosphere, Hg is oxidized slowly to Hg(II), with ozone (O_3) acting as the main oxidizer. Once oxidized, Hg(II) is scavenged from the atmosphere through precipitation or through adsorption to aerosol particles. Because of its long residence time in the atmosphere, its global distribution and subsequent precipitation, Hg can reach considerable concentrations in water and biota even in remote regions without any anthropogenic activity or natural deposits (Hall, 1995; Fitzgerald et al., 1998).

In aquatic systems, Hg(II) can be reduced to Hg(0) and evaporate because of such processes as photo-reduction. It can be present marginally as dissolved inorganic salts (chlorides or hydroxides), as organic complexes, or in the sediments. Under anaerobic conditions, it is precipitated as sulfides (HgS) and methyl groups are added according to bacterial or chemical methylation processes to form methyl mercury (MeHg), dimethyl mercury (Me_2Hg), or ethyl mercury (EtHg). The addition of these methyl groups significantly increases Hg's availability to biota; elemental Hg and the inorganic compounds are less bioavailable (Weber, 1993; Morel et al., 1998).

In low- and middle-income countries, Hg is released into the environment in part through the combustion of fossil fuels, but more significantly from its use in artisanal mining. It is used in this activity as a potent and relatively cheap agent for extracting gold via the amalgamation process. For instance, in North Sulawesi, Indonesia, in the Talawaan watershed where there is extensive artisanal gold mining, high concentrations of Hg were found in sediments, water systems, and aquatic species. Water samples of the Talawaan River contained maximum concentrations up to 0.014 mg Hg/L. These values exceed the EPA MCL for mercury in drinking water of 0.002 mg/L (United States Environmental Protection Agency, 2015c) by a factor of 7. In sediments, concentrations up to 22 mg/kg were found (Limbong et al., 2003). At the Wuchuan Hg mining site, Guizhou, China, high concentrations of between 79 and 710 mg Hg/kg were measured in mine wastes. In soils, concentrations ranging from 0.33 to 320 mg Hg/kg were found and water samples contained Hg concentrations up to 360 ng/L. A high average Hg concentration of 0.26 mg/kg was found in the vegetation. This amount exceeds the Hg concentration of 0.02 mg/kg recommended by the Chinese National Standard Agency for food sources (Qiu et al., 2006). In soils all over the world, the average Hg levels range between 0.58 and 1.8 mg/kg (Kabata-Pendias, 2010).

There is a body of evidence that Hg, particularly in the form of methylated Hg compounds, is accumulating among the food chain through biomagnification (Fergusson, 1990; Renzoni et al., 1998; Marrugo-Negrete et al., 2008). It has been shown that there is a positive correlation between increasing Hg concentrations in sediments and the amounts of Hg found in aquatic invertebrates and vertebrates. Generally, methylated Hg compounds accumulate mainly in the liver, kidney, brain, and muscles of benthic and predatory pelagic species. Because of this, these species represent the main sources of methyl Hg for humans (Renzoni et al., 1998). Eating fish and seafood with elevated levels of mercury causes adverse effects to human life (Harada, 1995; Castilhos et al., 2006). In addition, a positive correlation was found between the number of seafood meals eaten and the total mercury levels found in human hair (Harada, 1995; Renzoni et al., 1998; Olivero et al., 2002). According to a human health risk study, mercury concentrations in freshwater fish were investigated in the Tatelu region in Indonesia. In 154 fish of 10 freshwater species, a mean concentration of 0.58 ± 0.44 mg Hg/kg (wet weight) was measured. This is above the WHO guideline (World Health Organization and United Nations Environment Programme, 2008) of 0.5 mg Hg/kg in fish for human consumption (Castilhos et al., 2006). In the Talawaan watershed, nine of 47 fish muscle samples exceeded the safety level set for the international human consumption advisory limit (World Health Organization and United Nations Environment Programme, 2008). The highest concentration measured in fish in this region was 3.2 mg/kg (Limbong et al., 2003). In the Mojana region of Colombia, where gold mining activities are high, elevated concentrations of Hg, ranging from 0.043 to 0.512 mg/kg, were measured in different fish species. This is increasing the risk of mercury poisoning of the regional inhabitants for whom fish is part of their regular diet (Marrugo-Negrete et al., 2008). The elevated levels of mercury in fish indicate the high potency of Hg for bioaccumulation and biomagnification throughout the food chain.

The uptake of mercury into plants is relatively low; usually the natural mercury concentrations in plants are on a parts per billion level. The roots are usually the most predominant part for Hg accumulation, followed by the stems and leaves. According to one study of five arid-land riparian plants, between 2 and 11% of the mercury to which the plants were exposed was accumulated in the roots, between 0.2 and 3.36% in the stem, and between 0.3 and 0.94% in the leaves (Leonard et al., 1998). The level of Hg in the soil ranged from 23.8 to 53.5 mg/kg. It has been shown that plants can act as conduits for the interfacial transport of Hg from the geosphere to the atmosphere as a result of the uptake of Hg by the roots and assimilation of Hg(0) through stomata (Leonard et al., 1998). Additionally, it has been demonstrated that the uptake of organic Hg compounds is more prevalent than the uptake of inorganic ones (Huckabee and Blaylock, 1973).

Toxicity

Since the link was made that methylated mercury compounds were responsible for causing severe neurological disease in human in the Minamata area of Kyushu, the toxicity of mercury has been studied comprehensively (Harada, 1978). Given its high toxicity, the US EPA set the MCL of mercury in drinking water at 2 µg/L (Table 5) to protect public health (United States Environmental Protection Agency, 2015c). Also, mercury is a non-essential trace metal for plants and other biota (Adriano, 2001).

Generally, Hg(0) enters the human body as a result of ingesting pollutants in the workplace. Inorganic and methylated Hg compounds enter the human body as a result of consuming contaminated food and drinking water. After the pulmonary uptake of Hg(0), it is rapidly distributed within the body where it can cross both the placenta and the blood–brain barriers. If it is then oxidized to the mercuric ion, Hg(II), it will remain in the brain or placenta affecting human and fetal health. Non-oxidized Hg can be released from the body through exhalation, urine, sweat, saliva, or feces. The uptake of Hg(0) via the gastrointestinal (GI) tract is negligible, but between 7 and 15% of inorganic mercury compounds and from 90 to 95% of methylated mercury compounds are absorbed via the GI tract (Keating et al., 1997; Wolfe et al., 1998; Adriano, 2001). Inorganic Hg compounds have less of a tendency to pass the placenta and the blood–brain barriers, but methylated mercury compounds can easily pass through them. After gastrointestinal uptake, MeHg compounds bind to glutathione, cysteine, and other sulfhydryl-containing ligands that are secreted in the bile. Then these Hg compounds are reabsorbed in the gut entering the blood cycle. Here 90% are absorbed into the red blood cells and 10% are contained in the plasma. The binding of mercury to ligands with sulfhydryl groups promotes the transfer of MeHg compounds to the brain and throughout the placenta. The biological half-life of MeHg compounds in humans ranges from 44 to 80 days which can cause an accumulation of Hg in the human body. The ingested MeHg can be partly excreted through feces, breast milk, and urine (Adriano, 2001).

In humans and other animals mercury is a neurotoxin. Even at low doses it causes impairment of the nervous system. Typical symptoms of mercury poisoning are malfunctions of peripheral vision, numbness in the hands and feet, impairment of speech, hearing, and walking, mental degradation, and kidney damage. This is particularly the case for children born of mothers who have been exposed to mercury. Such children are very vulnerable and likely to suffer from mercury poisoning diseases, such as ataxia, constriction of the visual field, congenital cerebral palsy, and mental retardation (Agency for Toxic Substances and Disease Registry, 1999).

As well as humans, wildlife and the environment also show adverse effects from exposure to mercury. For instance, dietary concentrations of 4 to 5 ppm MeHg were lethal to small carnivores, like minks and ferrets, within 26 to 58 days (Wren et al., 1986; 1988). In some bird species, uptake by ingesting about 2 to 9 ppm is enough to cause impairments in reproduction. These are manifest as an increase in the number of shell-less eggs laid, decreases in the mean egg weight (Borg et al., 1970), and a decrease in egg production in general (Heinz, 1974). For different freshwater and marine algae species, Hg concentrations at a level of 0.1 ppm cause inhibition of growth. For the algae tested, inorganic mercury compounds seemed to be more toxic than the methylated ones (Hannan and Patouillet, 1972; International Agency for Research on Cancer, 2015). At the moment, no chronic environmental standard (AA-EQS) for aquatic organisms has been proposed.

Plants can act as conduits for the interfacial transport of Hg from the geosphere to the atmosphere.

In humans and other animals mercury is a neurotoxin. Even at low doses it causes impairment of the nervous system.

Group A: Thallium (Tl)

Introduction

Thallium (Tl) is a soft, malleable, bluish-white, non-essential metal. Thallium is contained mainly in potash minerals, in sulfides, in the ores of zinc, copper, and lead, and in coal (Kazantzis, 2000; Peter and Viraraghavan, 2005). The sulfide minerals lorandite and crooksite contain up to 60% Tl. Other sulfide minerals, like carlinite, christite, ellisite, weissbergite, galkhaite, vrbaite, and hutchinsonite, contain Tl as well (Peter and Viraraghavan, 2005). In nature, Tl can coexist with other substances like bromine, chorine, fluorine, and iodine and it can be found in sulfide minerals, which are used in gold (Au), Cu, Pb, Zn, and uranium mining (Twidwell and Williams-Beam, 2002). Thallium is found in the Earth's crust at concentrations ranging from 0.1 to 1.7 ppm (Kazantzis, 2000; Peter and Viraraghavan, 2005). In addition, granite and shale contain high amounts of Tl. This is especially so for shale and coal of the Jurassic period which contain highly elevated Tl concentrations – up to 1000 ppm (Smith and Carson, 1977).

In the past, Tl was used intensively in the agricultural and the medical sectors. Until the beginning of the 20th century, Tl salts were used widely to treat tuberculosis, venereal diseases, such as gonorrhea and syphilis, and malaria (DelValls et al., 1999; Kazantzis, 2000; Cvjetko et al., 2010). In addition, it was used as a depilatory in the treatment of ringworm of the scalp (Felden, 1928; Peter and Viraraghavan, 2005). Now, its use has been almost entirely abandoned in the medical sector because of its high acute toxicity (Léonard and Gerber, 1997). In agriculture and in private households, Tl salts were used extensively as insecticides and as a poison for rodents. Although, today, the use of Tl salts as pesticides (mainly thallium sulfates) has been banned in most countries because of their high acute toxicity, these salts are still in use in several low- and middle-income countries (Nriagu, 1998; Kazantzis, 2000)

Thallium is used mainly in the electronics, high-technology, and optical industries.

Nowadays, Tl is used mainly in the electronics, high-technology, and optical industries. It is used in low-temperature thermometers together with mercury and in scintillation counters, which are used to detect and quantify gamma radiation. It is used (together with Ca, Ba, Cu, and O_2) in electronic devices in the semiconductor and superconductor industries, in laser equipment (for medical imaging), in optical fiberglass, in optical lenses, in photovoltaic cells, and in infrared spectrometers (Zitko, 1975; Switzer, 1986; Galván-Arzate and Santamaría, 1998; Ramsden, 2002; United States Geological Survey, 2013). Moreover, it is used in the production of imitation jewelry, together with lead, zinc, silver, and antimony in alloys as anti-corrosion agents, for catalyzing organic reactions such as in the oxidation of hydrocarbons and olefins, for polymerization and for epoxidation, as a pigment in the dye and glass industries, and for impregnation of wood and leather to inhibit the formation of fungi and bacteria (Peter and Viraraghavan, 2005). Because Tl salts have a high acute human toxicity, and because Tl compounds are odorless and tasteless, Tl has acquired a reputation as an agent for criminal poisoning (Meggs et al., 1994; Rusyniak et al., 2002). In 2012, the global production of Tl by the mining sector was 10 tonne. This represents the smallest exploited amount of the metals of high environmental concern presented in this report (United States Geological Survey, 2013). However, it is estimated that between 2000 and 5000 tonne are circulated through industrial activities (Kazantzis, 2000).

The primary anthropogenic sources releasing Tl into the environment are flue dusts, vapors, and solid wastes emitted or discarded into the environment from brown coal and coal-based power generation plants. Thallium is released by the burning of coal in general, from cement production facilities, from the smelting of lead, copper, and zinc ores, and from steel and iron processing facilities. Many of these activities show an increasing trend. Mining activities, exploiting and extracting mineral sulfide ores, old tailings, and wastes from the electronics industry may act as considerable sources of Tl as well (Smith and Carson, 1977; Dolgner et al., 1983; Asami et al., 1996; Zhang et al., 1998; Kazantzis, 2000; Cheam, 2001; Lis et al., 2003; Nriagu, 2003; Stewart and Lemieux, 2003; Cvjetko et al., 2010).

Occurrence and behavior in the environment

Thallium occurs in two oxidation states – as monovalent Tl(I) and trivalent Tl(III). In the environment, Tl(I) is more stable and more common than Tl(III) (Adriano, 2001). In its chemical behavior, Tl(I) is similar to the alkali metal cation of potassium (K) (Zitko, 1975; Peter and Viraraghavan, 2005). Although these monovalent Tl compounds are relatively stable under certain conditions, Tl(I) salts – Tl(I) carbonates and Tl(I) sulfates – can be dissolved in water, reaching Tl(I) hydroxide concentrations up to 259 g/L. In this form, they become bioavailable to plants and biota (Dean, 1999; Zitko, 1975; Vink, 1993). In its chemical behavior, Tl(III) conforms to aluminum. It shows strong oxidizing properties and, in the environment, it is slowly converted to Tl(I) (DelValls et al., 1999). Tl(I) compounds are suspected of being more soluble and abundant than Tl(III) ones. However, it was found that Tl(III) compounds dominated in samples from a lake in Michigan. Between 68 and 74% of the total dissolved Tl compounds in the samples were Tl(III) ones. The reason for this is that Tl(I) was oxidized to Tl(III) by planktonic bacteria (Lin and Nriagu, 1999; Twining et al., 2003). These results show that there is a dearth of knowledge about the environmental behavior of Tl and that more investigations are required to better understand its distribution into the environment and its toxicity. In general, uncontaminated soils contain Tl concentrations of about 0.33 mg/kg (ppm; Asami et al., 1996). Seawater samples containdissolved Tl, the concentration ranging from 10 to 15 ng/L, and freshwater ones have concentrations of 5 to 10 ng/L (Flegal and Patterson, 1985; Cheam et al., 1995).

At high temperatures, the Tl compounds emitted are volatile. For this reason, they are not held back efficiently by electrostatic precipitators and other conventional filter systems and control facilities. Consequently, large amounts of Tl compounds are released into the environment through the burning of coal, smelting, and cement production processes involving sulfide ores (Ewers, 1988; Kazantzis, 2000). As a consequence, elevated environmental concentrations of Tl between 40 and 124 ppm are found in the Lanmuchang area of southwest Guizhou, China, in soil originating from the mining area (Xiao et al., 2004). Moreover, Tl accumulates in plants and biota. In the Lanmuchang area, China, elevated Tl concentrations in the range of 120 to 495 ppm dry weight (average 338 ppm) were found in green cabbage. In this region other plants, such as carrots, wild herbs, chili, rice, corn, and Chinese cabbage, take up considerable amounts of Tl as well (Xiao et al., 2004). In addition, lake trout from the Great Lakes in Michigan showed elevated average Tl concentrations of 0.141 ppm wet weight. This amount is comparable to the Tl amounts that have accumulated in brook trout, white sucker, and yellow perch in the Adirondack lakes, USA (Lin et al., 2001).

Toxicity

Even in industrial countries, information about the occurrence and the acute and chronic toxicity to humans, animals, and aquatic organisms is quite rare. For this reason, it is extremely difficult to assess the risk this metal poses to humans, other animals, and terrestrial and aquatic organisms in low- and middle-income countries (Peter and Viraraghavan, 2005). Nevertheless, a small number of toxicity studies indicate that Tl is highly toxic and not essential for humans and other mammals. It affects the health of invertebrates and plants as well. According to IARC, Tl has not been classified as a compound which causes cancer in humans. Currently, few toxicity studies are available and no significant link has been found that the uptake of Tl promotes the formation of cancers (International Agency for Research on Cancer, 2015). For mammals, it is suspected that the toxicity of Tl exceeds that of the heavy metals Hg, Cd, Pb, and Cu (Cheam, 2001). Because of that, Tl is on the list of priority pollutants of the US EPA (United States Environmental Protection Agency, 2014c). In addition, EPA defines the MCL as 0.002 mg/L (Table 5; United States Environmental Protection Agency, 2015c). The global limits for Tl concentrations in crops are from 0.03 ppm to 0.3 ppm (dry mass) and those for land plants are 0.008 to 1 ppm (dry mass; Kabata-Pendias, 2010).

The uptake of Tl happens when contaminated food and drinking water is ingested. Thallium aerosols can be taken up by inhalation; Tl can also be absorbed through contact with the skin mucous membranes. This latter ingestion process occurs mainly as a result of occupational exposure. Given its similarity in ionic charge and its ion radius to potassium, Tl, especially Tl(I), can be absorbed and easily distributed throughout the body by mimicking potassium in its movement patterns and intracellular accumulation in mammals. In the body, it accumulates in bones, the renal medulla, and the nervous system. The excretion of Tl occurs mainly through urination. However, it is excreted in breast milk, sweat, and saliva as well (Zitko, 1975; International Programme on Chemical Safety, 1996; Hoffman and Hoffman, 2000; Peter and Viraraghavan, 2005). A dose of between 0.7 and 1.1 g of soluble Tl salts is considered to be the minimum lethal dose for an adult with a body weight of 70 kg (Moeschlin, 1980). The symptoms of acute Tl poisoning are alopecia, nausea, tachycardia, diarrhea, and impairment of the lungs, heart, and gastrointestinal system. Impairment of the nervous system is more likely a result of chronic exposure to Tl, but there is a lack of studies about the regular chronic uptake of low doses of Tl (Saddique and Peterson, 1983; Agency for Toxic Substances and Disease Registry, 2013; Frattini, 2005; Cvjetko et al., 2010). The toxicity of Tl to humans and other mammals is based on the interference of Tl(I) with vital potassium-dependent processes. Since K(I) and Tl(I) have similar ion charges and ion radii, the cell membrane is not able to distinguish between them. For instance, Tl substitutes for potassium in the Na^+/K^+-ATPase. In addition, given its affinity for the sulfhydryl groups of proteins and mitochondrial membranes, Tl inhibits a range of enzyme reactions causing adverse effects and poisoning (Ramsden, 2002). Furthermore, Tl is able to pass the blood–brain and placenta barriers, affecting the nervous system and causing impairments in the growth and development of fetuses (Hoffman and Hoffman, 2000; Tsai et al., 2006).

Reliable data about the toxicity of Tl to organisms of environmental relevance are quite rare. Nevertheless, investigations show that the acute toxicity of fish to Tl is comparable to that of copper.

Reliable data about the toxicity of Tl to organisms of environmental relevance are quite rare. Nevertheless, investigations show that the acute toxicity of fish to Tl is comparable to that of copper. According to this, concentrations ranging from 0.03 to 60 mg/L are lethal for different fish species. For aquatic invertebrates, like daphnia and gammarus, lethal concentrations of 2 to 4 mg/L were found. For mice, an LD_{50} dose of between 16 and 27 ppm (effective dose) was reviewed in a paper by Zitko (1975). According to the chronic environmental standard (AA-EQS), it is estimated that concentrations above 0.013 µg Tl/L can adversely affect the health of water organisms (Staatscourant, 2010).

Group B: Antimony (Sb)

Introduction

Antimony (Sb) is a bluish-white, brittle, and glossy metalloid (Fowler and Goering, 1991). Antimony can be found in the environment as sulfides and complex Cu-Sb, Pb-Sb, and Hg-Sb sulfides and oxides. The sulfides stibnite and antimonite and the oxide valentinite are the most important commercially used ores. In addition, coal and petroleum contain relevant amounts of Sb (Adriano, 2001; Filella et al., 2002). In the Earth's crust, Sb occurs in concentrations of around 0.2 and 0.3 ppm (Fowler and Goering, 1991).

Antimony is used in semiconductors and is contained in detectors, diodes, and Hall-effect devices – used for measuring magnetic fields – batteries, small arms and tracer bullets, cable sheathings, antifriction alloys, and in alloys to increase the hardness and the mechanical strength of lead. It is used also in car brakes (Filella et al., 2002; Iijima et al., 2007, 2008). The Sb oxide Sb_2O_3 is used in large amounts as a flame retarding additive in textiles, papers, and plastics. It is a component of some adhesives. Also, it is used as a pigment in paints, as a catalyst, as a mordant, and in the ceramic and glass industry (Filella et al., 2002; United States Geological Survey, 2013). In addition, Sb_4O_8 is used commonly as an oxidation catalyst for the oxidative dehydrogenation of olefins (Filella et al., 2002). Antimony is used in medicaments for the treatment of tropical protozoan diseases like leishmaniasis, schistosomiasis, ascariasis, and trypanosomasis (Filella et al., 2002). According to the data of the US geological survey, 180,000 tonne of antimony were mined in 2012 (United States Geological Survey, 2013).

There is evidence that exposure to Sb compounds from anthropogenic causes exceeds that from natural sources. The primary sources of Sb are smelting and refining facilities, energy producing plants that burn fossil fuels, waste incineration plants, mining, and vehicles. In the latter, Sb is present in abrasion materials from tires, brakes, and motor bearings (Fowler and Goering, 1991; Newton et al., 1994). Data from 1988 to 1990 show that, annually, about 3500 tonne of Sb originated from anthropogenic sources, while 2600 tonne were emitted through natural sources, such as volcanic activities, salty sea spray, and forest fires. However, since then, primary Sb production has increased from 138,000 to 180,000 tonne, which may have lead to higher anthropogenic emissions of Sb aerosols (Nriagu and Pacyna, 1988; Nriagu, 1989, 1990a; Maeda, 1994).

Occurrence and behavior in the environment

In the environment, Sb occurs mainly in the oxidation states III and V. In soils, background concentrations of around 1 to 10 ppm have been measured (Shacklette and Boerngen, 1984; Hammel et al., 2000; Reimann et al., 2010). In unpolluted freshwater systems, it can be found at concentrations of less than 1.0 µg/L (Reimann et al., 2010), and the oceans contain even smaller amounts of Sb, concentrations below 200 ng/L being reported (Filella et al., 2002). Although Sb is widely used in large quantities, little attention has been drawn to this metalloid. Accordingly, there is little information available about the transformation and distribution processes of Sb and its different compounds among the different environmental compartments. However, as far as it is known, Sb occurs mainly as sulfides and sulfidic complexes, oxides, and hydroxides. It also occurs in the environment as the more volatile methylated species (Filella et al., 2002; Wilson et al., 2010). Since 1990, the obligatory implementation of filter systems for incineration plants, smelters, metal refining facilities, and energy generating plants has led to a decrease in the amount of organic and inorganic pollutants emitted, especially in HICs. However, since these filter systems are not mandatorily applied in all low- and middle-income countries, and large quantities of Sb are still mined there, the emissions of Sb and other metalloids or heavy metals in these regions are reaching levels of environmental concern. For instance, samples collected from Prestea, a gold mining town in West Ghana, showed elevated Sb concentrations in water ranging from 0.09 to 0.75 mg/L and in soils ranging from 8.5 to 90.4 ppm (Serfor-Armah et al., 2006).

In the Abaróa Sb mine area in southern Bolivia, heavy rainfalls have caused severe erosion of tailings dumps, releasing large amounts of inorganic pollutants, such as Pb, Zn, and Sb, into the Rio Chilco-Rio Tupiza drainage system. There, sediments between the Rio Abaróa and the Rio Machocuya, contained an average 341.9 mg Sb/kg (ppm) and the sediments of the adjacent floodplains had Sb concentrations of about 37.40 ppm (Villarroel et al., 2006). In addition, soils at one of the world biggest Sb mining and smelting areas in Hunan, China, had elevated Sb concentrations of up to 5045 ppm (He, 2007).

There is evidence that Sb is bioavailable for plants. However, these results differ a lot from each other and for different plant species. For instance, the leaves and shoots of endive, corn salad, spinach, biennial parsley, and carrot leaves accumulated from just 0.6 to 1% of Sb from the surrounding soil. The soil originates from a historical mining site and contains Sb concentrations of 54.4 to 67.0 ppm (Hammel et al., 2000). In contrast, the leaves of radish plants at a mining site and in the vicinity of smelting facilities accumulated up to 10.8% Sb (the soil concentration was measured at 852 mg Sb/kg (ppm; He, 2007). These differences indicate that knowledge about the uptake of Sb compounds is still raising questions. Most of the studies do not discriminate between the uptake via roots or the adsorption of Sb aerosols onto the epicuticular waxes on the plant surfaces. Therefore, it is difficult to predict the uptake of Sb by the roots (Ainsworth et al., 1990a; He, 2007; Tschan et al., 2009). Tschan et al. investigated by exposing different plant species to 25 µmol/L $KSb(OH)_6$ solutions. It was found that the shoots of sunflowers take up and accumulate Sb to about 24 ppm dry weight, those of perennial ryegrass 17 ppm dry weight, those of wheat 16 ppm dry weight, and those of maize 3 ppm dry weight (Tschan et al., 2009). These results show that plants are able to take up Sb compounds via their roots, although the uptake varies by an order of a magnitude among the different plant species. Under these experimental conditions, the bioavailability of less water-soluble Sb species, such as Sb sulfides and Sb oxides, would be less pronounced than the uptake of the more water soluble Sb hydroxides and KSbO tartrates (Hammel et al., 2000). In contrast, Ainsworth et al. reported that the contamination of vegetation is more likely related to continuing atmospheric deposition than to uptake from the soil (Ainsworth et al., 1990a).

In general, Sb shows a low or no tendency for bioconcentration throughout the food chain (Filella et al., 2002). Although in fish samples near the Sb mining area in Hunan, China, Sb concentrations of up to 218 ppb were measured (Fu et al., 2010), there is evidence that Sb concentrations in ground-living invertebrates are lower than the concentrations in their diets. There is evidence also that the Sb content in the tissue of small mammals is less than that of their dietary intake (Ainsworth et al., 1990b).

Toxicity

Although Sb apparently does not accumulate in the food chain, there is evidence that it has a high toxic potential and that it is not essential for plants, humans, and animals (Adriano, 2001). The IARC has classified antimony trioxide as a Group 2b compound possibly carcinogenic to humans. Antimony trisulfide has not been classified as to its carcinogenicity to humans (International Agency for Research on Cancer, 2015). According to the US EPA, Sb and Sb compounds are considered as priority pollutants and its drinking water standard, called MCL, is 6 µg Sb/L (Table 5; United States Environmental Protection Agency, 2014c, 2015c). In addition to the other metals and metalloids of environmental concern in this report – As, Cd, Pb, Hg, Tl, hexavalent Cr, and Cu compounds – Sb is listed as a hazardous substance because of the Basel Convention restriction on its transfer across borders (United Nations Environment Programme, 2014). In general, organoantimonials, like methylated Sb compounds, are the least toxic. Pentavalent Sb compounds are increasingly so and trivalent Sb compounds show the highest toxic potential (particularly Sb_2O_3; Gebel, 1997; He and Yang, 1999; Krachler et al., 2001). For mammals, there is evidence that trivalent compounds have a clastogenic, but not mutagenic, activity. Rats were exposed through inhalation to 45 mg/m^3 of Sb_2O_3 and Sb ore concentrate. While the male rats were not affected, 27 (25%) of the females developed lung neoplasms (Groth et al., 1986). However, controversial results are found as well. For instance, the findings of Elliott et al. did not confirm that exposing rats to Sb_2O_3 caused genotoxic or clastogenic effects (Elliott et al., 1998). Thus, there is still not sufficient evidence available to determine whether Sb compounds have carcinogenic effects on humans or not (Gebel, 1997). Nevertheless, the Occupational Safety and Health Administration (OSHA) defined the permissible exposure limit at 0.5 mg Sb/m^3 as a time-weighted average concentration over an eight hour working shift (National Institute for Occupational Safety and Health, 1988a).

In plants, an exposure to 30 mg/L caused significant inhibition in root growth in maize and wheat compared to the control. In addition, exposure to just 3 mg Sb/L led to an inhibition, though not significant, in shoot biomass (Tschan et al., 2009). According to the AA-EQS, chronic aquatic concentrations above 7.2 µg/L can adversely affect the health of water organisms (Marion Junghans (Ecotox Centre); personal communication).

Group B: Arsenic (As)

Introduction

Arsenic (As) is a brittle, steel-grey, crystalline metalloid. Like Sb, it is found primarily in sulfide deposits as arsenides, sulfides, and sulfosalts, often together with Ag, Pb, Cu, Ni, Sb, Co, Fe, Zn, and Au (Adriano, 2001; International Agency for Research on Cancer, 2012b). The most prevalent As-containing minerals are arsenian pyrite ($Fe(S,As)_2$), arsenopyrite (FeAsS), löllingite ($FeAs_2$), realgar (AsS), orpiment (As_2S_3), cobaltite (CoAsS), niccolite (NiAs), and scorodite ($FeAsO_4$ x $2H_2O$; Wang and Mulligan, 2006; Smedley and Kinniburgh, 2013). In the Earth's crust it occurs at concentrations between 1.5 and 2 ppm (Salomons and Förstner, 1984; Luoma and Rainbow, 2008).

Historically, inorganic and organic arsenic compounds were used as pesticides, insecticides, fungicides, and soil sterilizers. They were used also as medicaments to treat several spirochetal and protozoal diseases and parasites, and other diseases, such as leukemia, psoriasis, and chronic bronchial asthma. Until now, several As compounds were used in the veterinary sector to treat animals infected with parasites. Arsenic compounds are used also as wood preservatives in non-residential areas (Adriano, 2001; Wang and Mulligan, 2006; Agency for Toxic Substances and Disease Registry, 2007a; International Agency for Research on Cancer, 2012b). However, today, most arsenic-based agricultural and pharmaceutical agents are being phased out because of restrictions related to their high toxic potential (Adriano, 2001; United States Environmental Protection Agency, 2009). Arsenic compounds are used as pigments in the ceramic, tanning, and glass industries and the metal form is used as an additive in lead and copper alloys, ammunition, the grids of lead–acid storage batteries, optical, and infrared devices. Gallium arsenide semiconductors are used in the electronics industry in solar cells, space research, and telecommunication (Adriano, 2001; Bissen and Frimmel, 2003; United States Geological Survey, 2013). In 2012, around 44,000 tonne of arsenic trioxide (AS_2O_3) was produced worldwide. This is the main arsenic compound that enters end-product manufacturing (Adriano, 2001; United States Geological Survey, 2013).

The primary man-made sources of As contamination of the environment are the combustion of coal and oil containing traces of arsenic, orphan mining sites, inappropriately-closed mines, and residual tailings. Waste incineration, disposal of e-waste, and ore refining and smelting processes (especially lead and copper ores) are other significant point sources of arsenic (World Health Organization, 2001; Wang and Mulligan, 2006; International Agency for Research on Cancer, 2012b; United States Geological Survey, 2013).

Occurrence and behavior in the environment

Since arsenic contamination of groundwater has been reported worldwide, anxieties concerning arsenic-related problems have increased (Mukherjee and Bhattacharya, 2001; Wang and Mulligan, 2006; Centeno et al., 2007; Amini et al., 2008). Accordingly, natural contamination by As, through the weathering, leaching, and erosion processes of arsenic-containing rocks and soils, volcanic activity, and natural fires, is of high environmental concern. Within the scope of our report, we focus more on anthropogenic arsenic contamination.

Natural arsenic concentrations in surface waters, such as rivers and lakes, barely exceed 0.01 mg. The oceans and groundwater have average As concentrations around 1 to 0.002 mg and the background concentrations in soils are about 5 mg/kg (World Health Organization, 2001).

Elevated As concentrations, ranging from 3.6 to 295.1 mg/kg, have been found in soil samples in the mining and smelting area of Hunan, China, and concentrations of 942 to 10,200 mg/kg have been found near the gold mining town of Prestea, Ghana, (Serfor-Armah et al., 2006; He, 2007). In Hunan, As concentrations up to 0.0113 mg were detected in water samples and in Prestea the concentrations in the water samples measured 8.25 mg/L (Serfor-Armah et al., 2006; Fu et al., 2010).

The physicochemical properties of As are comparable to those of Sb, but arsenic compounds are much more toxic and more easily bioavailable to plants and invertebrates (Gebel, 1997; Tschan et al., 2009; Fu et al., 2010; Wilson et al., 2010). Similarly to Sb, As occurs mainly in two oxidation states – as trivalent (arsenite) and pentavalent (arsenate) arsenic compounds in the environment. The reduced trivalent compounds are more likely to occur under anaerobic conditions and the pentavalent ones under aerobic ones (International Agency for Research on Cancer, 2012b). Organic arsenic compounds, such as arsines and methylarsines, mostly are unstable in air if they are not absorbed and accumulated by plants and other biota or adsorbed to organic matter (Adriano, 2001; Centeno et al., 2007; Tschan et al., 2009).

In general, adsorption processes to soil and the leaching processes of As compounds from soils depend on several biogeochemical factors, such as particle size, soil composition, organic matter content, nature of constituent minerals, pH, water hardness, redox potential, oxygen, calcareous content, and the number of competing ions (Goldberg and Glaubig, 1988; Masscheleyn et al., 1991; Jones et al., 2000; Adriano, 2001; Smith et al., 2002; Yamaguchi et al., 2011). Generally, it can be said that As(III) is less strongly adsorbed to soil than As(V). Thus, trivalent As compounds are more mobile and, thus, more toxic than As(V) compounds. This increased mobility of As is enhanced because of the reduction of arsenate to arsenite (Masscheleyn et al., 1991; Chiu and Hering, 2000).

There is still a lack of knowledge related to the sorption and mobilization processes of As compounds. There is evidence that in each case they can be mobilized under reducing or oxidizing conditions. On the one hand, under anaerobic aquatic conditions, As(III) is more likely to be mobilized because of reductive dissolution. It has to be said that, in the presence of higher sulfate concentrations, the release of As is hindered, mainly because of microbial-dependent sulfate reduction or surface arsenic adsorption, resulting in the precipitation or incorporation of arsenic compounds in sulfides (Bostick and Fendorf, 2003; Rowland et al., 2006; Amini et al., 2008). On the other hand, under aerobic environmental conditions in arid and semi-arid regions with high evaporation rates and resulting higher salinity, arsenate (AsO_4^{3-}) and other anions are less strongly adsorbed to mineral surfaces and, therefore, are more water soluble (Amini et al., 2008; Smedley and Kinniburgh, 2013).

After the mobilization of As into aquatic media, As compounds can be taken up by plants and other biota. Naturally, plants and aquatic organisms do not incorporate enough As to be toxic to humans, so it seems that As does not accumulate in the food chain. Often, before reaching internal As concentrations that are toxic to humans, the plants suffer from phytotoxic effects leading to inhibition of growth or crop failure. Also it seems that As negligibly bioaccumulates in fish (National Academy of Sciences, 1977; Eisler, 1994; Adriano, 2001; Jones, 2007).

However, contradictory evidence has been found as well. For instance, in areas with extremely high As contaminations, such as near smelting and waste incineration facilities and in areas with a high level of mining activity, As may indeed have the potency to accumulate throughout the food chain (Tamaki and Frankenberger Jr, 1992; Wang and Mulligan, 2006; Agency for Toxic Substances and Disease Registry, 2007a). In addition, the investigations of Tschan et al. show that plants are accumulating arsenic (around three times more easily than Sb). In the shoots of plant seedlings of perennial ryegrass, As concentrations of 58 mg/kg dry weight have been measured after exposure to 1.9 mg As/L for one week. The corresponding value for wheat is 43 mg/kg dry weight, for sunflowers, 36 mg/kg dry weight, and for maize 4 mg/kg dry weight (Tschan et al., 2009). In addition, rice grains collected from mine-affected areas in Hunan, China, had levels of inorganic As up to 624 µg/kg, which is four times higher than that of the vast majority of rice grains on the rice market (Zhu et al., 2008). In barley, wheat and rice, As concentrations of the order of 100 µg/kg up to 10.2 g/kg have been measured. For rice, the amount of As transferred and accumulated in the shoots is even higher (1.5 to 20.6 g/kg) than the amount of As found in the soil (5 to 10 g/kg), indicating that rice is able to bioaccumulate As (Williams et al., 2007). In fish near the mining area in Hunan, elevated As concentrations of up to 152 µg/kg wet weight have been measured (Fu et al., 2010). In addition, considerable concentrations of As in the range of µg/kg to g/kg have been found in food samples (National Academy of Sciences, 1977; Jones, 2007). Whether accumulating through the food chain or not, arsenic poses a risk to environmental and human health because of its high acute toxicity even at low concentrations.

Toxicity

Similarly to Sb compounds, the toxicities of arsenic compounds conform to the following order, from least to highest: organoarsenicals (methylated species), arsenates (pentavalent As), and arsenites (trivalent As; Nriagu, 1994). IARC has listed inorganic As compounds as Group I carcinogens for humans, while organic As compounds are classified in Group III, not carcinogenic for humans (International Agency for Research on Cancer, 2015). The MCL, which represents the highest level of the contaminant that is allowed in drinking water, as determined by the US EPA, is 0.01 mg (Table 5; United States Environmental Protection Agency, 2015c). The uptake of As occurs mainly from eating contaminated food and drinking contaminated water. It can also occur from occupational exposure through the inhalation of pollutants at coal-fired power plants, mining areas, waste incineration, smelting, and battery assembly facilities. It can also be taken up via the mucous membrane and percutaneously (Eisler, 1994; Agency for Toxic Substances and Disease Registry, 2007a; International Agency for Research on Cancer, 2012b). The acute minimal lethal dose of inorganic As is estimated to be between 70 and 200 mg (Caravati, 2004). The symptoms of acute As poisoning are stomach ache, nausea,

The uptake of As occurs mainly from eating contaminated food and drinking contaminated water. Chronic ingestion of As-contaminated drinking water has resulted in significant negative consequences for human health.

vomiting, and diarrhea. Furthermore, acute uptake of As can cause a decrease in the production of red and white blood cells, cardiac arrhythmias, and blood-vessel damage resulting in bruising, and impaired nerve function (Agency for Toxic Substances and Disease Registry, 2007a). With their high acute toxicity and their being odorless, colorless, and tasteless, As salts have been used historically as suicidal and homicidal agents, particularly during the Middle Ages (Smith, 2013). In the long term, a daily chronic exposure to 0.02 mg/kg by ingestion can lead to adverse health effects in sensitive humans (Ontario Ministry of the Environment, 2001). In addition, chronic (20 years) ingestion of As-contaminated drinking water with a concentration of 0.13 mg As/L, has resulted in significant negative consequences for human health (Lerda, 1994). Chronic poisoning symptoms are peripheral neuritis, gastritis, enteritis, liver and kidney failure, cardiac dysfunctions, melanosis, depigmentation, hyperkeratosis, and several forms of cancer (Niu et al., 1997; Mazumder, 2000; Adriano, 2001; Mead, 2005). After uptake, arsenic compounds are effectively assimilated via the gastrointestinal (GI) tract. For instance, in the GI tract 60% of the ingested As(V), 80% of the As(III), and 100% of organoarsenicals are adsorbed after ingestion (Zielhuis and Wibowo, 1984; Gebel, 1997). In short, the toxic effects of inorganic As are a result of their affinity for and ability to bind with sulfhydryl groups, such as glutathione and metallothionein. The results of this binding are alterations of the protein structures, which consequently cause disruptions of metabolic processes. Following the bonding to sulfhydryl groups, metabolic processes, such as cellular glucose uptake, fatty acid oxidation, and production of glutathione, can be affected (Gochfeld, 1997). Arsenic compounds are not directly mutagenic; however, they do behave clastogenically, which means that they give rise to or induce disruptions in or breakages of chromosomes (Jha et al., 1992; Lerda, 1994). In this context, As does not directly interact with DNA: its genotoxic effects are induced indirectly through alterations of gene expression by impairment of DNA methylation, induction of oxidative stress, and changes in the regulation of signal transduction pathways (Gebel, 1997; Kitchin and Ahmad, 2003).

From an environmental perspective, As compounds, such as monosodium methylarsonate, disodium methylarsonate, and dimethylarsinic acid, are known for their phytotoxic effects. Consequently, they have been broadly used as herbicides (Bissen and Frimmel, 2003). In general, for most plants a depression in crop yield results after exposure to soils having concentrations of water soluble As from 3 to 28 mg/L and total arsenic concentrations from 25 to 85 mg/kg (Furlong, 1978; Eisler, 1994). In addition, after exposure of 1.9 mg As/L, wheat, maize, perennial ryegrass, and sunflower seedlings have suffered a significant reduction in biomass, ranging from 48 to 20%. (Tschan et al., 2009). The investigations of Eisler revealed that for aquatic invertebrates, concentrations of 0.019 to 0.049 mg As/L in water for invertebrates, concentrations of 120 mg As/kg in diets, and for algae, concentrations of 1.3 to 5 mg As/kg fresh weight in tissues, provoke significant health-damaging effects and, therefore, pose a risk to environmental health (Eisler, 1994). From an environmental perspective and according to the proposed chronic environmental quality standard (AA-EQS), the concentration of As in aquatic systems should not exceed 0.05 mg/L in the long term to guarantee the welfare of water organisms (UK Technical Advisory Group on the Water Framework Directive, 2008).

Group C: Asbestos

Introduction

Asbestos is the commercially used collective noun for a group of naturally occurring silicate minerals with fibers that are long, thin, and flexible when separated (Stayner et al., 2013). Asbestos minerals can be separated into two groups. These are serpentine minerals, classified as sheet minerals because the silicate (SiO_4) tetrahedrons are serialized as sheets, and amphibole minerals, classified as chain silicates because the SiO_4 tetrahedrons are organized as a double chain of two rows (International Agency for Research on Cancer, 2012c; Stayner et al., 2013). The most abundant chrysotile asbestos is an asbestos mineral belonging to the serpentine group found as veins in serpentine rocks. The asbestos minerals actinolite, amosite, anthophyllite, crocidolite, and tremolite are characteristic amphibole minerals (International Agency for Research on Cancer, 2012c). In ambient air, asbestos compounds are naturally found in concentrations ranging from 0.00001 to 0.0001 fibers/mL (Agency for Toxic Substances and Disease Registry, 2008).

With their physicochemical characteristics of high tensile strength, flexibility, resistance to chemical and thermal degradation, and high electrical resistance, asbestos minerals are useful for a wide range of industrial applications (National Toxicology Program, 2014a; International Agency for Research on Cancer, 2012c; United States Geological Survey, 2013).

Asbestos fibers can be used in the textile industry. With their heat resistance and high insulating properties, they are used in packing materials for steam glands on high-temperature machines and insulation for boilers, steam pipes, and electrical wiring. Asbestos fibers are used in fireproof paints, for suits and blankets, in fireproof construction materials for walls, floors, and roofs, and as additives in asphalt road surfaces. Asbestos-cement is used in the mass production of cheap, fireproof building materials and asbestos-cement pipes are widely used as water and waste pipes. Furthermore, they are used in the automobile industry in brakes, clutch components, and engine gaskets, in the millboard industry, and in filters. The decreased level of production of asbestos in the 1990s is attributable to the finding that exposure to asbestos is associated with the occurrence of lung cancer (Selikoff and Lee, 1978; Tomatis et al., 1978; Agency for Toxic Substances and Disease Registry, 2001; Virta, 2006; International Agency for Research on Cancer, 2012c).

In 2003, the use of asbestos was banned or restricted in 16 countries – Argentina, Austria, Belgium, Chile, Denmark, Finland, France, Germany, Italy, the Netherlands, Norway, Poland, Saudi Arabia, Sweden, Switzerland, and the United Kingdom. By 2005, the use of asbestos was almost completely banned within the European Union. Until now, the use of asbestos has been restricted or banned in 57 countries (Virta, 2006; International Ban Asbestos Secretariat, 2015). Nevertheless, although asbestos minerals are banned in several countries, the world mining production of 2 million tonne/year indicates that asbestos is still in use. For instance, the US EPA has generated a list of products containing asbestos that are still produced (United States Geological Survey, 2013; United States Environmental Protection Agency, 2015d). In addition, there is evidence that the use of asbestos, especially in many developing countries, is increasing (Stayner et al., 2013).

Although asbestos minerals are banned in several countries, the world mining production of 2 million tonne/year indicates that asbestos is still in use.

The modern industrial use of asbestos started around 1880 and peaked in 1975 with an estimated world production of 5.09 million tonne. However, during the last decades worldwide mining production of asbestos has declined and reached a plateau at around 2 million tonne (International Agency for Research on Cancer, 2012c; United States Geological Survey, 2013).

Asbestos fibers, clumps of asbestos and asbestos dust enter the air, aquatic, and terrestrial environments naturally as a consequence of the weathering and erosion of natural deposits and asbestos-bearing rocks. The primary source of asbestos mineral pollution is a result of anthropogenic activities. Open-pit mining operations, crushing, screening, milling of ore, and all the processes involved in extracting, processing, and manufacturing asbestos are man-made sources of asbestos fibers. Furthermore, inappropriate disposal of waste material containing asbestos, corrosion of asbestos-cement pipes, other asbestos materials used in the construction sector, and the abrasion of asbestos from asphalt or vehicle brakes, clutches, and engine gaskets are additional sources releasing asbestos fibers into the environment (Selikoff et al., 1972; Millette et al., 1980; Williams and Muhlbaier, 1982; Cheng and O'Kelly, 1986; Agency for Toxic Substances and Disease Registry, 2001; Abratt et al., 2004).

Occurrence and behavior in the environment

At the moment, data about environmental asbestos and non-occupational concentrations are quite limited. Nevertheless, there is evidence that significantly elevated concentrations of asbestos can be found in water supplies. Concentrations above 1 million fibers/L have been found in the drinking water of 18% of the 406 cities tested in Puerto Rico and the District of Columbia (Millette et al., 1980). In the Castro Valley Bay area, California, USA, asbestos concentrations of up to 319 million fibers/L have been measured in runoff samples. Creek sediments contained asbestos concentrations up to 230 million fibers/L and street surface particles had concentrations of up to 1300 million fibers/L (Pitt, 1988). In 2012, in the USA alone, 7300 tonne of friable asbestos were reported to have been released by 41 facilities, according to data of the Toxics Release Inventory (TRI) program (United States Environmental Protection Agency, 2012). Data about the release of asbestos in low- and middle-income countries is in short supply (Stayner et al., 2013). However, in these countries, occupational exposure to asbestos minerals is still a big issue, especially when obsolete techniques for mining and processing asbestos minerals are used and if the handling of asbestos products takes place without proper precautions (Ramanathan and Subramanian, 2001). For example, in an asbestos processing mill in Andhra Pradesh, India, maximal asbestos concentrations of up to 488,050 fibers/L were measured. This despite the legal level allowed for asbestos production in this region being set below 2000 fibers/L (Ramanathan and Subramanian, 2001).

Toxicity

All asbestos minerals cause cancer and are potentially toxic. The primary uptake routes for asbestos in humans are by ingesting contaminated food and water and by inhaling asbestos aerosol particles during handling (repacking of asbestos containers, transport, and disposal), processing (dry cutting, milling, and production of construction material), and the use of asbestos-containing raw materials and products. Uptake via the respiratory system seems to be the most hazardous and relevant one. In addition,

All asbestos minerals cause cancer and are potentially toxic. The primary uptake routes for asbestos in humans are by ingesting contaminated food and water and by inhaling asbestos aerosol particles.

people who are living in the vicinity of asbestos mining sites and manufactories, and people living in houses containing asbestos products in the floors, roofs, and walls are taking up elevated amounts of the material and posing risks to their health (World Health Organization, 2006; International Agency for Research on Cancer, 2012c).

The uptake of the acerous, sharp asbestos fibers causes a range of diseases, such as asbestosis (fibrosis of the lungs), mesothelioma, and several other forms of cancer of the pharynx, larynx, esophagus, lungs, stomach, and colorectum, and the thickening of pleural plaques and effusions. These diseases have a long latency (Selikoff et al., 1964; Doll and Peto, 1985; International Programme on Chemical Safety, 1985; Enterline et al., 1987; Selikoff and Seidman, 1991; World Health Organization, 2014; Landrigan et al., 1999; National Research Council, 2006; World Health Organization, 2006; International Agency for Research on Cancer, 2012c). Thus, if the use of asbestos is eliminated right now, the number of asbestos-related deaths will decrease only after a few decades (World Health Organization, 2006).

It is estimated that globally around 125 million people are exposed to asbestos in their occupations. Of these, 90,000 people are estimated to die annually from asbestos-related diseases (World Health Organization, 2006). Given their high toxicity, all asbestos minerals are classified by the IARC as Group I carcinogens for humans. For drinking water, the limiting value of asbestos contamination, referred to as MCL, is 7 million fibers/L (Table 5; United States Environmental Protection Agency, 2015c). In occupational settings, the permissible limits for asbestos range between 100 fibers/L and 2000 fibers/L as a time-weighted average for a normal eight hour workday and a 40 hour week (National Institute for Occupational Safety and Health, 1988b; International Agency for Research on Cancer, 2012c). Nevertheless, it seems that in several regions, especially in low- and middle-income countries, regulations controlling and monitoring human and environmental exposure to asbestos are lacking, posing risks to human and environmental health (Giannasi and Thébaud-Mony, 1997; Joshi and Gupta, 2003; Virta, 2006; LaDou et al., 2010). According to the literature, it is feared that the continuous use of asbestos in low- and middle-income countries will trigger an epidemic of asbestos-related diseases, such as mesothelioma and lung cancer in the near future (Joshi and Gupta, 2004; LaDou et al., 2010; Stayner et al., 2013).

From an environmental toxicological point of view, there have been few investigations of the negative impacts of asbestos on aquatic and terrestrial animals following exposure to anthropogenically released asbestos minerals. However, histological examinations of blue mussels, exposed to waste products containing 10 mg/L of asbestos for five days, indicated that asbestos particles can be taken up and afterwards remain in the gastrointestinal tract causing significant tissue injuries (Halsband, 1974). Further investigations showed that vertebrates – lake trout – incorporate asbestos fibers particularly into their kidneys and, less pronouncedly, into their muscle tissue. In contrast, other fish species, such as catfish, brook trout, and Arctic char, showed a lower potential to incorporate asbestos minerals. The proposed hypothesis to explain this was that the uptake of asbestos minerals is more dependent on eating behavior and the food intake than on uptake via the gill system (Batterman and Cook, 1981). In addition, although asbestos minerals can be incorporated into fish, they seem not to accumulate in the food chain because the asbestos concentration in muscle tissue is half the external water concentration (Batterman and Cook, 1981). Exposure tests on Coho salmon and green sunfish showed that asbestos concentrations of about 1.5 million to 3.0 million fibers/L are enough to cause behavioral stress effects, like impairments in rheotaxic position and balance. Although a destructive effect of asbestos on lateral line histology was observed – this is responsible for the loss of rheotaxic position – the mortality did not increase significantly after exposure to asbestos at the concentrations tested (Belanger et al., 1986). There is evidence that the release of asbestos can affect environmental health. According to the most recent status report, environmental risk assessment is not possible, especially in low- and middle-income countries, where almost no data about environmental asbestos concentrations are published. Nevertheless, a chronic environmental standard (AA-EQS) of 7 million fibers/L was proposed (United States Environmental Protection Agency, 1999).

Table 5: Data about hazardous heavy metals, metalloids, and minerals from the mining industry

Name[A]	Primary production [tonne] (United States Geological Survey, 2013)	Most toxic species	Potentially toxic to (Adriano, 2001)	Maximum Contaminant Level (MCL) (United States Environmental Protection Agency, 2015c) [mg/L]	Environmental quality standard AA-EQS/MAC-EQS [µg/L][B]
Metals					
Cadmium →	23,000 with 54% produced in low- and middle-income countries	Cd(II) (Adriano, 2001)	Plants, animals, humans	0.005	Class 1: 0.08/0.45 Class 2: 0.09/0.6 Class 3: 0.15/0.9 Class 4: 0.25/1.5[C] (European Parliament and Council of the European Union, 2008)
Chromium →	24 million with 94% produced in low- and middle-income countries	Cr(VI) (International Agency for Research on Cancer, 2012d)	Plants, humans, animals (Mishra and Mohanty, 2008)	0.1	Cr(III): 4.7/32 Cr(VI): 3.4/NA (UK Technical Advisory Group on the Water Framework Directive, 2008)
Copper ↑	17 million with 42% produced in low- and middle-income countries	Cu(II), $CuOH^+$, $[Cu_2(OH)_2]^{2+}$ (Flemming and Trevors, 1989)	Plants, animals (aquatic organisms) (Richardson, 1997; Borkow and Gabbay, 2005; United States Environmental Protection Agency, 2008; Vardy et al., 2014)	1.3	1/NA (based on the bioavailable concentration) (UK Technical Advisory Group on the Water Framework Directive, 2012)
Lead ↑	5.2 million with 67% produced in low- and middle-income countries	Pb(II) (Agency for Toxic Substances and Disease Registry, 2007b)	Plants, animals, humans	0.015	1.2 (based on the bioavailable concentration)/14 (European Parliament and Council of the European Union, 2013)
Manganese ↑	16 million with 76% produced in low- and middle-income countries	$Mn(VII)O_4^-$ (Young et al., 1996), Mn(II, III) oxides, $Mn(II)SO_4$, $Mn(II)Cl_2$ (United States Environmental Protection Agency, 2010)	Plants	NA (WHO limiting value 0.4) (World Health Organization, 2004)	123/NA (UK Technical Advisory Group on the Water Framework Directive, 2012)
Mercury ↓	1,600 with 92% produced in low- and middle-income countries	MeHg, Me_2Hg (Weber, 1993; Morel et al., 1998; Wolfe et al., 1998)	Animals, humans	0.002	NA (but biota standard is 20 µg/kg wet weight)/0.07 (European Parliament and Council of the European Union, 2013)
Thallium →	10 (proportion produced in low- and middle-income countries not definable)	Tl(I), $Tl(I)_2SO_4$, $Tl(I)_2CO_3$ (Zitko, 1975; International Programme on Chemical Safety, 1996; Hoffman and Hoffman, 2000; Cheam, 2001; Peter and Viraraghavan, 2005)	Plants, animals, humans	0.002	0.013/0.8 (van Vlaardingen and Verbruggen, 2009)
Metalloids					
Antimony →	180,000 with 97% produced in low- and middle-income countries	Sb(III); $Sb(III)_2O_3$, Sb(V) (Gebel, 1997; He and Yang, 1999; Krachler et al., 2001; International Agency for Research on Cancer, 2015)	Animals, humans	0.006	7.2/NA (Marion Junghans (Ecotox Centre; personal communication)
Arsenic ↓	44,000 with 73% produced in low- and middle-income countries	As(III), As(V) (Nriagu, 1994)	Plants, animals, humans	0.01	50/NA (UK Technical Advisory Group on the Water Framework Directive, 2008)
Minerals					
Asbestos ↓	2 million with 48% produced in low-and middle-income countries	Fibers (Agency for Toxic Substances and Disease Registry, 2001)	Animals, humans	7 million fibers/L	7 million fibers/L (United States Environmental Protection Agency, 1999)

A: *🟠 Decreasing use trend; 🟡 Use trend is unsure – approximation is difficult; 🟢 Increasing use trend (United States Geological Survey, 2013; Barrientos and Soria, 2013).*

B: *The acute and the chronic environmental quality standards (EU-standard), AA-EQS (annual average concentration) and MAC-EQS (maximum allowable concentration) represent chronic and acute environmental concentrations of chemical agents which affect water organisms significantly.*

C: *AA-EQS and MAC-EQS of cadmium are dependent on water hardness classes: Class 1: < 40 mg $CaCO_3$/L; Class 2: 40 to 50 mg $CaCO_3$/L; Class 3: 50 to 100 mg $CaCO_3$/L; Class 4: 100 to 200 mg $CaCO_3$/L.*

Input pathways of mining pollutants

The lifetime of a mine depends on the main material being mined and the stocks of the ores and minerals of interest. Thus the lifetime can be several years or several decades, even as long as a few centuries (International Council on Mining & Metals, 2012). Uneconomical mines can be closed inappropriately, especially in low- and middle-income countries, with nobody assuming responsibility for the orphan mining sites. Often the authorities do not have the capacity to remediate contaminated regions. At abandoned mining sites, the chemical or bacterial oxidation of iron pyrite or other sulfidic minerals results in acidified mine water effluents, causing acid mine drainage (AMD). These acidified mining effluents contain high concentrations of dissolved heavy metals and metalloids, of which arsenic, cadmium, copper, and lead are of the highest concern. These effluents endanger water resources and the environment. AMD occurs particularly in flooded mining sites, waste rock dumps, tailings, and piled heaps of proceeded material (Johnson and Hallberg, 2003, 2005; Farrell et al., 2004).

Acidified mining effluents contain high concentrations of dissolved heavy metals and metalloids, of which arsenic, cadmium, copper, and lead are of the highest concern.

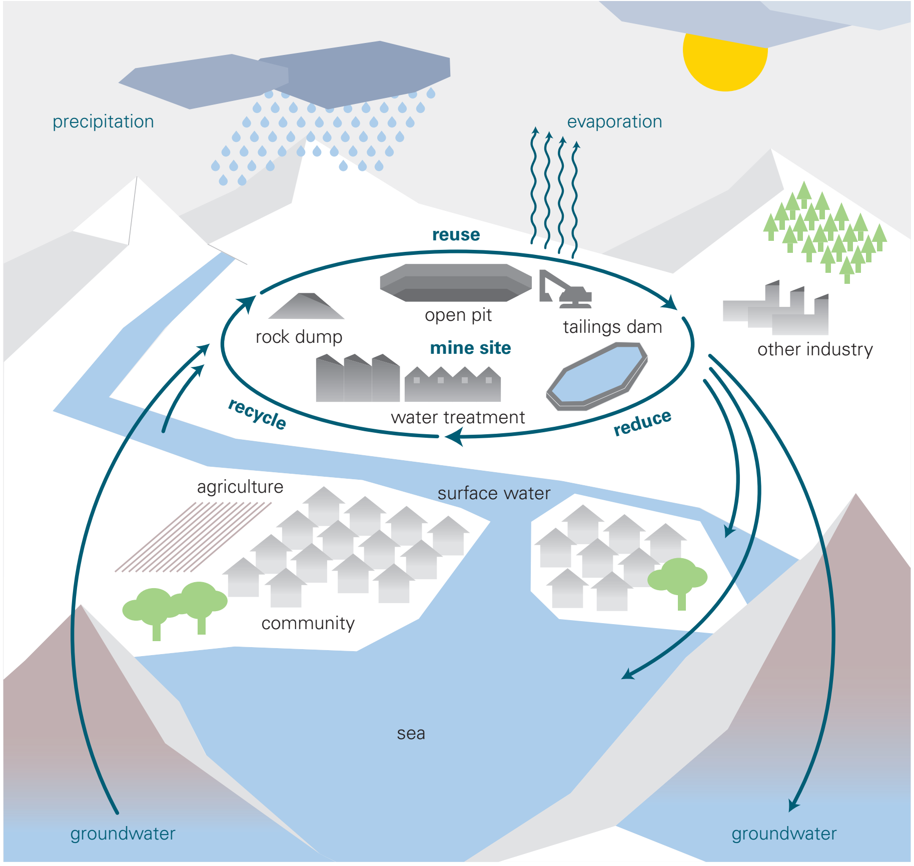

Figure 19: *Mining-related water cycle (International Council on Mining & Metals, 2012)*

AMDs and other untreated mining wastewater, slag, solid waste, and tailings can be discarded inappropriately into surface waters or left uncovered next to the mining site (Blacksmith Institute and Green Cross, 2012). These abandoned mining wastes, with their high contents of acids and toxic heavy metals, pose risks to environmental and human health. From these mining wastes, toxic compounds can leach into groundwater aquifers, lakes, and river systems through surface runoff. In low- and middle-income countries, these contaminated water sources are often used for irrigation, thus degrading valuable and fertile agricultural land (He, 2007; Figure 19).

In addition, during ore exploitation, transport, and extraction, and the processing and refining of ores and minerals, hazardous pollutants and metals can be released into the environment.

Social impacts of mining

Since the Industrial Revolution, and as a result of the further developments and progress made in the technical industrial sector, the extraction of metals, metalloids, and minerals has been indispensable for meeting resource needs. The mining industry is a viable way for achieving a rapid and profitable economic revival in the short term (International Institute for Environment and Development, 2002; Low, 2012).

To date, the mining sector has made little contribution in terms of sustainable development (International Institute for Environment and Development, 2002). In addition, although this sector is associated with social and economic benefits, it is known for its ruthless approaches that cause environmental destruction and disadvantage society (Farrell et al., 2004). Today, the mining industry is under pressure to improve its environmental and social performance. From this perspective, the social impacts of mining are emphasized in this report (Miranda et al., 2003).

On the one hand, as already mentioned, there are some social benefits that result from mining (Table 6). The extraction of resources can lead to a rapid and temporary economic boom, result in an increase of gross domestic product, and create new jobs. Furthermore, mining is often associated with the setting up or improvement of infrastructure, such as roads, hospitals, living quarters, telecommunication systems, and water supplies. These are needed to enable the transport and refining of the exploited raw materials and to accommodate and supply the mine workers (Miranda et al., 2003; Farrell et al., 2004)

On the other hand, mining comes with a list of disadvantages and negative social impacts (Table 6). The mining sector is a heavy user of energy and water. Indeed, the mining sector is one of the most energy-intensive of all industries. It consumes approximately 7 to 10% of global energy production each year. In addition, while it is common knowledge that mining requires a lot of water during the exploitation, extraction, and refining processes, the global volume of water that flows through this industry has not been estimated yet (Farrell et al., 2004). Also, mining can cause the destruction of valuable living environments for humans and wildlife. Mining activities are often associated with deforestation, the dredging of huge pits, the disposal of waste rocks, acids, and ores, and the possible formation of AMD. In this sense, one-quarter of the World Heritage Sites are at risk from the extractive industries, including mining and oil and gas extraction. Deforestation can have secondary consequences, such as increasing surface runoff and the erosion of sediments, which result in suspended sediment loads in surface waters and floods of increasing frequency (Miranda et al., 2003; Farrell et al., 2004). Additionally, mining often causes severe pollution of soils or water bodies, groundwater, and other drinking water sources.

These events contribute to the degradation of agricultural land and drinking water resources. Previously established and longstanding traditional businesses, such as agriculture and fisheries, which are indispensable to the lives of local people, are often affected as well. An increasing shortage of water and the degradation of arable land provoke tensions between farmers, miners, and other local inhabitants by increasing their competitiveness. Furthermore, the local people often lack accurate information about the effects of mining. Moreover, there is evidence that mining is responsible for the displacement and resettlement of local inhabitants. This can provoke riots and violence, causing a general public discomfort or even civil wars (Downing, 2002; Terminski, 2012).

There are several international initiatives to promote more environmentally-friendly and ethically reasonable mining. These initiatives include the World Summit on Sustainable Development (WSSD), the Mining, Minerals and Sustainable Development (MMSD) project, the Extractive Industries Review of the World Bank, and the International Council on Mining and Metals (ICMM). They involve implementing best practices in those regions, mostly in low- and middle-income countries, where regulations are poorly implemented. Informal artisanal and small-scale businesses seem to be of particularly high relevance (Miranda et al., 2003; Swenson et al., 2011; Low, 2012). In these regions, there are less controls and monitoring studies of the hazardous toxicants that are released into the environment by the mining and other sectors. Often, poor approaches to waste management and waste and protective clothing are other problems, related to mining. In low- and middle-income countries the frequency of occupational accidents far exceeds that in higher-income ones (Miranda et al., 2003; Farrell et al., 2004).

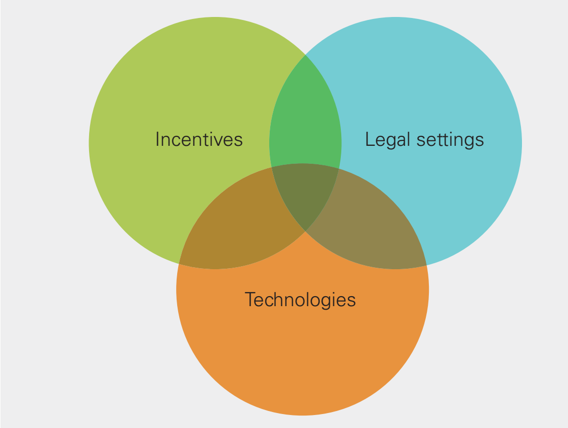

Figure 20: *Venn diagram of the basic modules enabling more environmentally-friendly mining*

In general, viable economic incentives from government, consultants, and NGOs, acceptable legal settings from politicians, decision makers, and local authorities, and proper technologies need to be applied in the mining industry to enable the more sustainable, environmentally-friendly, and ethically reasonable exploitation and processing of metals, metalloids, and minerals (Figure 20).

The mining sector is a heavy user of energy and water.

Mining activities are often associated with deforestation, the dredging of huge pits, the disposal of waste rocks, acids, and ores, and the possible formation of Acid Mine Drainage.

Table 6: Short overview of the social benefits and detriments of mining activities (Miranda et al., 2003; Farrell et al., 2004)

Social benefits	Social detriments (not best practices approaches ^{A})
• Temporary economic boom • Setting up and/or improvement of infrastructure	• High consumption of energy and water by the mining sector • Destruction of valuable living environments for humans and wildlife • Severe pollution of soils and water bodies, groundwater, and and other drinking water sources, affecting human and environmental health. Previously established and longstanding traditional economic sectors, such as agriculture and fisheries, which are indispensable to the lives of local people, are often affected • Displacement of local people, causing general public discomfort

A: Efforts, initiatives, and best practices are implemented to reduce the negative social impacts which tend to accompany mining activities. Nevertheless, there is evidence that such best practice approaches are not yet available and feasible worldwide, which leads to the significant list of social detriments mentioned here

Production and pollution trends of hazardous metals, metalloids, and minerals

Data availability

At present there are two comprehensive public databases available that address the primary production of metals, metalloids, and minerals. One is a compendium of world mining data from the 'Austrian 'Federal Ministry of Economy, Family and Youth' and the 'International Organizing Committee for the World Mining Congresses' (Reichl et al., 2013). The other is the data from the 'Mineral Commodity Summaries, 2013' (United States Geological Survey, 2013), developed by the United States Geological Survey (USGS). For this report, the USGS data were used because they are used and mentioned more frequently in scientific literature and have been compiled since 1996.

Future trends and hot spots

According to the USGS data presented in Table 5, it can be seen that the primary production of copper, lead and manganese has increased until the last few years. The exploitation of cadmium, chromium, thallium, and antimony through mining has plateaued while the primary production of mercury, arsenic, while asbestos has decreased during the last years.

Figure 21 shows the sum of the mined metals, metalloids, and minerals of highest concern to environmental and human health that are discussed in this report – antimony, arsenic, asbestos, cadmium, chromium, copper, lead, manganese, and mercury. The primary production of gold is also included because often large quantities of mercury are still used for gold extraction as can be seen in Figure 23. For thallium, no comprehensive data were available (Castilhos et al., 2006; Artisanal Gold Council, 2015; Barrientos and Soria, 2013; United States Geological Survey, 2013). Figure 21 shows the areas of potential risk in low- and middle-income countries. These are the places where the highest amounts of hazardous metals, metalloids, and minerals are mined. They include South Africa, China, Kazakhstan, India, Brazil, Gabon, Peru, Indonesia, Zambia, where Mexico and production volumes range from 670,000 to 14 million tonne.

For a broader perspective, Figure 22 shows the sums of the primary production of minerals and/or ores:

(A) Used for industrial purposes. These include asbestos, barite, boron, diamonds, diatomite, feldspar, fluorspar, graphite, kaolin, magnesite, perlite, phosphates, potash, salt, sulfur, talc, vermiculite, and zircon

(B) Iron and ferro-alloy metals. These include iron, chromium, cobalt, manganese, molybdenum, nickel, tantalum, titanium, tungsten, and vanadium

(C) Non-ferrous metals. These include aluminum, antimony, arsenic, bauxite, bismuth, cadmium, copper, gallium, germanium, lead, lithium, mercury, rare earth minerals, tellurium, tin, and zinc.

The latest available data for each commodity for the period 2010–2012 are used (Soria, 2013; United States Geological Survey, 2013).

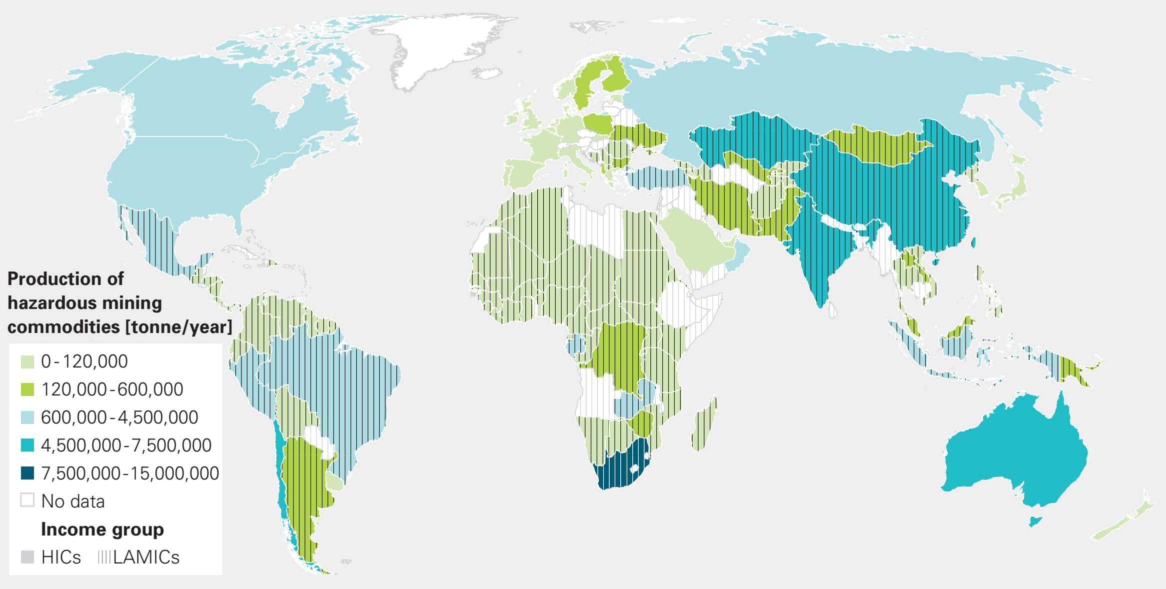

***Figure 21**: World primary production (tonne/year) of heavy metals, metalloids, and minerals of highest concern to environmental and human health. These include antimony, arsenic, asbestos, cadmium, copper, chromium, gold, lead, manganese, and mercury (Barrientos and Soria, 2013; United States Geological Survey, 2013)*

These data show that in low- and middle-income countries, such as China, Morocco, India, Brazil, Iran, Mexico, Egypt, Turkey, and Chile, the largest amounts of industrial commodities are produced by primary production. The countries are listed in descending order of production. Primary production ranges from 12 million to 210 million tonne. Iron and ferro-alloy metals, in particular, are mined in low- and middle-income countries like China, Brazil, India, South Africa, Ukraine, Kazakhstan, and Iran. Production volumes range from 13 to 330 million tonne. China, Brazil, and India mined the highest amounts of commodities used in the non-ferrous metal industry; outputs ranged from 20 to 69 million tonne.

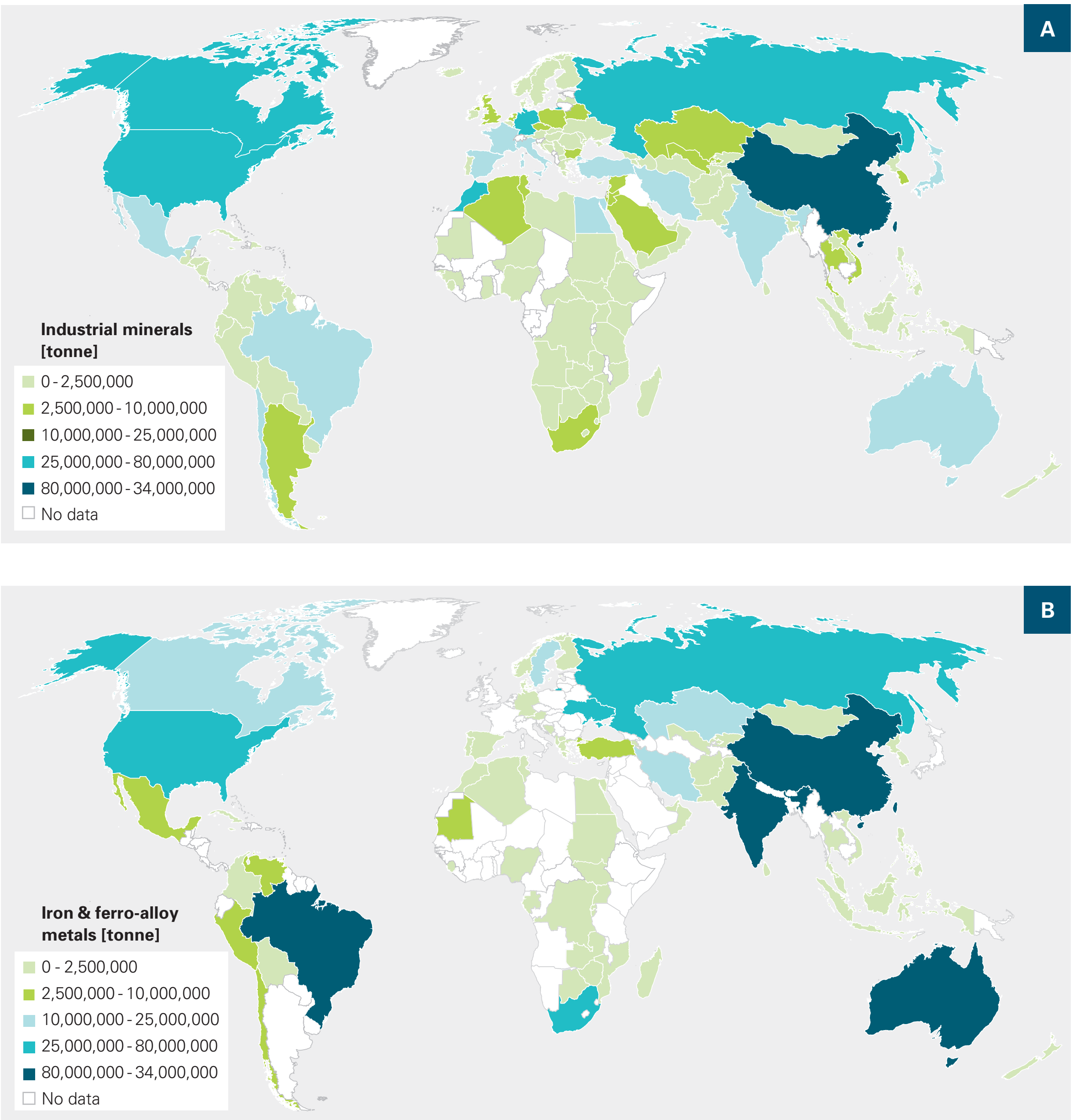

Figure 22: *Extraction [tonne] of industrial minerals (Barrientos and Soria, 2013; United States Geological Survey, 2013)*

A: Asbestos, barite, boron, diamonds, diatomite, feldspar, fluorspar, graphite, kaolin, magnesite, perlite, phosphates, potash, salt, sulfur, talc, vermiculite, and zircon

B: Iron, chromium, cobalt, manganese, molybdenum, nickel, tantalum, titanium, tungsten, and vanadium

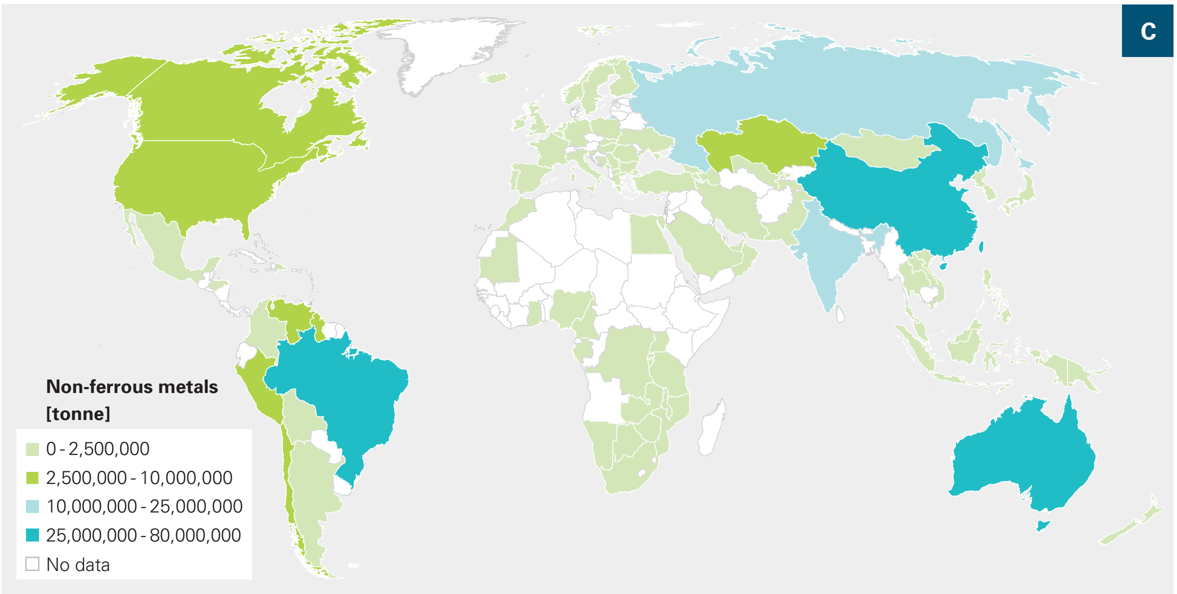

Figure 22: *Extraction [tonne] of industrial minerals (Barrientos and Soria, 2013; United States Geological Survey, 2013)*

C: Aluminum, antimony, arsenic, bauxite, bismuth, cadmium, copper, gallium, germanium, lead, lithium, mercury, rare earth minerals, tellurium, tin, and zinc

Issues of special concern

Artisanal small-scale mining

One of the biggest environmental problems related to mining in low- and middle-income countries is that of informal artisanal and small-scale mining (ASM). ASM activities are known for their large-scale risks (Farrell et al., 2004; Artisanal Gold Council, 2015). Given the informal nature of this business, a reliable assessment of annual gold production through ASM is not possible. However, it has been estimated that about 10–15 million people are engaged in ASM and that about 12–30% of the gold on the world market comes from ASM activities (Farrell et al., 2004; United Nations Environment Programme, 2008; Telmer and Veiga, 2009). ASM, in the main, uses obsolete production methods including the amalgamation technique. In this technique, large amounts of mercury are used to extract the gold. (To extract one unit of gold, three units of mercury are required (Telmer, 2011). Often, these miners are poor. They have few resources to invest in pollution control devices. They are poorly educated in mining and they have little awareness of the hazards of mercury or the other chemical agents used for the extraction of metals from ores (United Nations Environment Programme, 2008). Commonly, these miners are organized in small collectives or they work with their families to extract gold and other precious metals. In the latter case, the women and children are at highest risk because often the amalgamation is done by them at home while the men dig for ores. There is evidence that the mercury used for extraction is handled with bare hands and normal cooking equipment is used (Farrell et al., 2004; Low, 2012). Furthermore, the unregulated disposal of mercury pollutes soils and water (Malm, 1998; van Straaten, 2000; Limbong et al., 2003; Telmer and Veiga, 2009). In addition to the potential for environmental pollution, ASM has acquired a bad reputation for its support of child labor (Kippenberg, 2011). In several regions, parents send their children to work in the mines, risking their lives to increase the family income. Moreover, often the artisanal and small-scale miners are paid very little for the gold extracted; it is the traders and local officials who make the big profits (Kippenberg, 2011).

Figure 23 shows that artisanal and small-scale gold mining pose a large-scale risk. For instance, in the low- and middle-income countries of Mongolia, Guyana, Venezuela, Democratic Republic of the Congo, Burkina Faso, Tanzania, Brazil, Ecuador, Peru, Philippines, Colombia, Indonesia, and China, from 10 to 445 tonne (mean values) of mercury are released each year by artisanal gold mining activities (Artisanal Gold Council, 2015).

Acid mine drainage at abandoned mining sites

In active and, more likely, in abandoned open-pit mines, open underground shafts, and at sites where tailings have been dumped, the formation of acid mine drainage (AMD) is a very serious environmental pollution problem (Naicker et al., 2003; Kalin et al., 2006). AMD is mainly the result of sulfide rocks (mainly pyrite and marcasite) and sulfide rich tailings being exposed to oxygen and water (moisture in the air, rainwater, surface water, and groundwater) and several abiotic and biotic oxidation processes (Johnson and Hallberg, 2003; Kalin et al., 2006). Whereas in active mines, the groundwater is pumped out in order

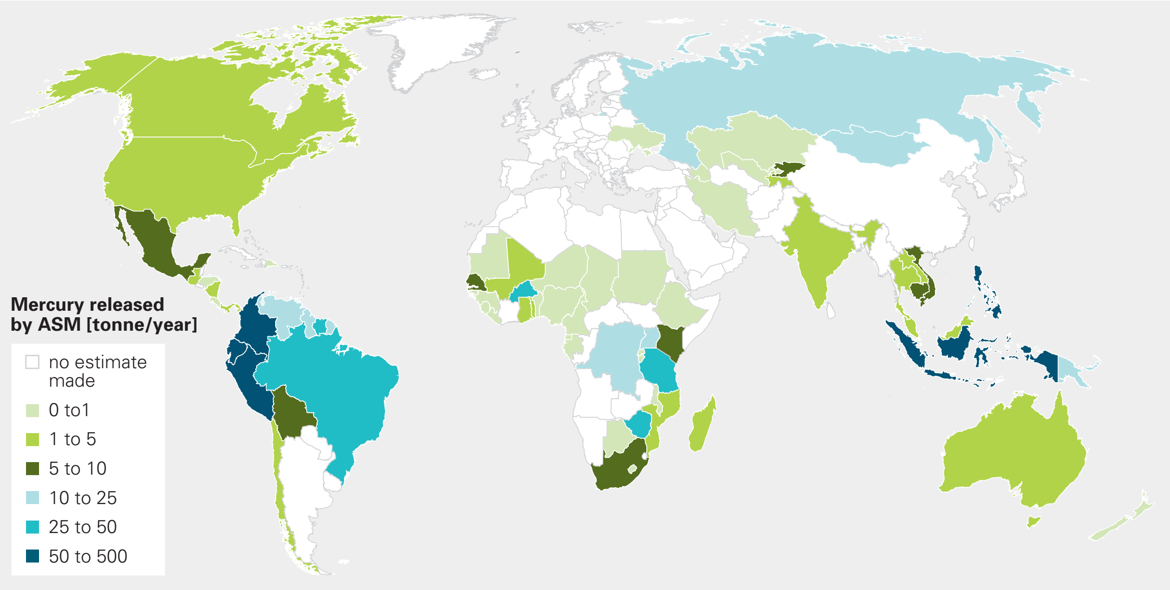

***Figure 23**: Amount (tonne) of mercury released by artisanal gold mining (mean values) (Artisanal Gold Council, 2015)*

to mine the ores, in abandoned mines, when the pumps are turned off, the water table rises. This, in the presence of oxygen and of sulfide rocks, results in AMD (Johnson and Hallberg, 2005). If these sulfides are oxidized in the presence of water, sulfuric acid is produced. These acidic drainages (AMDs) leach into the soil and migrate with surface and groundwater streams. With their low pH they provoke the release of several heavy metals and metalloids associated with sulfide rocks. These include antimony, arsenic, cadmium, copper, iron, mercury, manganese, lead, thallium, and zinc (Schwartz, 2000; Adriano, 2001; Filella et al., 2002; Naicker et al., 2003; Peter and Viraraghavan, 2005). The chemical processes involved in the formation of AMD are:

1. The oxidation of iron sulfide
2. Ferrous iron (Fe^{2+}) oxidation
3. Ferric iron (Fe^{3+}) hydrolysis
4. The enhanced oxidation of ferric sulfide ions.

$$FeS_2 + {}^{7}/_{2}O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

$$Fe^{2+} + {}^{1}/_{4}O_2 + H^+ \longrightarrow Fe^{3+} + {}^{1}/_{2}H_2O \qquad (2)$$

$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3(s) + 3H^+ \qquad (3)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \longrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (4)$$

This oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) and the production of sulfuric acid, and thus the formation of AMDs, can be accelerated by acidophilic bacteria and archaea (Johnson and Hallberg, 2003). Today, especially in low- and middle-income countries, the remediation techniques for AMD polluted sites are still too costly and labor intensive. If untreated, AMD can pose an environmental burden for thousands of years (Farell et. al., 2004).

Investigations in the Witwatersrand region of South Africa, which is famous for its gold mining, have measured highly elevated levels of heavy metals and metalloids in surface water, groundwater, and soil samples near abandoned tailings. As a result of AMD, concentrations in the order of mg/L have been found for chromium, zinc, cadmium, lead, copper, iron, manganese, cobalt, nickel, sodium, and calcium, and in the order of µg/L for arsenic, mercury, and selenium (Naicker et al., 2003). At this mining site, acidified and heavy metal contaminated groundwater and seepage waters with even lower pHs have resulted from AMD, causing high levels of environmental pollution. Although not mentioned in the literature cited before, in the same region, the leaching of uranium from soils through AMD causes environmental damage of high concern (Winde and de Villiers, 2002; Winde and Sandham, 2004; Tutu et al., 2008). In the Natalspruit River, downstream from the mining area, the river beds were coated with a layer of orange colored limonite that has been deposited over decades. The result is that this river is no longer a habitat for animal life; and only a minimal amount of aquatic vegetation can be found in this region (da Silveira et al., 2009). Examples of AMD like this can be found worldwide. However, in low- and middle-income countries, it is those regions with few environmental controls, restrictions, regulations, and resources for remediation, and where abandoned mines and tailings are left in unsafe conditions that are affected the most (Djenchuraev, 1999; McKinnon, 2002; Lin et al., 2007; Blacksmith Institute and Green Cross, 2013).

Working conditions and occupational incidents

In higher-income countries, the mining and ore refining industries have made considerable progress in providing safer work environments and in using more environmentally-friendly methods (Blacksmith Institute and Green Cross, 2012). In low- and middle-income countries, some progress has been made as a result of initiatives of the 'Strategic Approach to International Chemicals Management' (SAICM) policy framework and the 'International Council on Mining and Metals' (ICMM). However, inadequate enforcement of environmental legislation and lack of environmental restrictions and controls result in the release of toxicants into the environment. Besides the adverse effects caused to the environment, the health of the employees in the mining and ore refining sectors is endangered as well. According to the report 'The World's Worst Pollution Problems, 2012', in lower-income countries, the health of 2.5 million people engaged in the lead smelting industry and of 14 million people involved in the mining and ore processing industries is at risk (Blacksmith Institute and Green Cross, 2012).

For instance, there is evidence that bad working conditions have been found in Chinese-run copper mines located in Zambia (Smith, 2011). There, employees are working under poor, unhealthy, and unsafe conditions (inadequate ventilation and insufficient protective clothing). The workers are put under continuous pressure and exploited, having labor shifts of 12 to 18 hours. From medical examinations of and personal interviews with the workers, there is evidence that the employees suffer considerably from diseases associated with mining pollutants because of the bad and unsafe working conditions. Additionally, the mine workers were urged to keep secret any occupational incidents (Wells, 2011). It can be assumed that it is not just these miners in Zambia who are working under unsafe and unhealthy conditions.

Best practices

Implemented examples

Increasing data transparency

Regrettably, corruption within the mining and mineral sector is still a significant issue. This is particularly the case where mining activities have expanded in the lightly-regulated and remote regions of low- and middle-income countries, like Southeast Asia, South America, and Africa (Marshall, 2001; McEwen, 2011; Ernst & Young, 2012). The Extractive Industries Transparency Initiative (EITI) was established to increase transparency of the global revenue from extractives, such as petroleum and mining products, among all participating companies, governments, and civil societies. The EITI is a global coalition of governments, companies, and civil societies that is acting as a global standard for improving the openness and accountable management of revenues from natural resources. To discourage corruption, the EITI standards require the full disclosure of taxes and other payments made by oil, gas, mineral, and mining companies to governments. These payments are publicly available in an annual report (Extractive Industries Transparency Initiative, 2015).

Joining EITI can be beneficial for all participants of the multi-stakeholder group. For instance, by implementing the EITI standards, governments demonstrate commitment to reform and to dealing with corruption. This can lead to improved tax collection. The companies benefit from an enhanced and more stable investment climate because all companies are required to disclose the same information. This enables an improved engagement with citizens and society. Citizens and civil society benefit by receiving reliable information and the established multi-stakeholder platform improves the interactions between the different stakeholders (Extractive Industries Transparency Initiative, 2015).

In the extractive sector, enhanced transparency concerning revenues and improved transparency in the material flow of mining products are required. This will help provide more detailed economic information about exports and imports, which, in turn, leads to a better understanding of global supply chains in minerals, metalloid, and metals. Beside its economic relevance, this information can be used to estimate the amounts produced and refined on regional and international scales. For instance, the USGS is providing international and comprehensive data about the production, import, and export of minerals, but its data concerning the trade of minerals (exports and imports) is more referenced to the situation in the USA (United States Geological Survey, 2013). With the information of the EITI and the USGS, it may be possible to assess regions with a high potential for corruption and where mining can pose risks to environmental and human health.

Sustainable mining

Huge quantities of water are required during ore processing. The water is used for dust suppression, transporting slurry, and the needs of employees. Hence responsible approaches to water management and the implementation of water recycling systems are mandatory. By so doing, valuable water resources can be retained, the release of mining pollutants into surface water and groundwater can be reduced, and competitiveness between the mining industry and other interested groups, such as fisheries, farmers, and local municipalities, can be diminished. Conscientious use of water resources by mining industries is an important criterion for ensuring continued sustainability of mining operations. This is especially the case in water-stressed regions – to the extent that one can talk about sustainability and mining operations in the same breath. Accordingly, the ICMM is focusing on improving the industry's water management performance (International Council on Mining & Metals, 2012).

There are several case studies addressing improvement of water management mentioned in the ICMM report 'Water management in mining: a selection of case studies' (International Council on Mining & Metals, 2012). For example, in the coal mining region near the city of Emalahleni, northeast South Africa, where water resources are rare, the Emalahleni Water Reclamation Plant (EWRP) was commissioned in 2007. With the help of the EWRP, it is possible to treat water from mining operations and to pump and treat water from orphan mines. Following this treatment, an additional supply of water can be delivered from the plant to the local municipality's drinking water system. This reduces social water stress and retains drinking water resources. In addition, by pumping water out of abandoned mines, the formation of AMD and the additional dissolving of hazardous metals, metalloids, and salts can be prevented (International Council on Mining & Metals, 2012).

Remediation techniques

Taking the necessary precautions and avoiding causing environmental pollution from the outset is cheaper and more sustainable than environmental remediation. Nonetheless, more time and money should be invested to find feasible and low cost remediation techniques that can be implemented, particularly in already contaminated regions in low- and middle-income countries. Currently, there are several methods for remediating sites contaminated with inorganic pollutants (e.g. hazardous metals and metalloids). These include:

- The isolation method, which uses physical barriers made of steel, cement, and bentonite, and ground walls to immobilize pollutants

- The solidification/stabilization method, which injects agents to encapsulate contaminants in a solid matrix, or reduces the mobility of the contaminant by forming chemical bonds

- The size selection method, which separates larger cleaner particles from smaller more polluted ones

- Electrokinetic processes, which, by using low-intensity electric currents, precipitate ions and small charged particles that are then transported by water

- Bioleaching, which uses bacteria under aerobic conditions to leach out metals and metalloids (an effect comparable to the one forming AMD)

- Phytoremediation and constructed wetlands, which uses non-edible and disease-resistant plants, or plants which can provide renewable energy, that are able to take up and incorporate heavy metals and remove them from soils and contaminated water systems

- Soil washing and in-situ flushing, which is achieved by adding water, organic or inorganic acids, sodium hydroxide, water soluble solvents, and complexing agents in various combinations.

Most of these techniques are feasible and implemented only in industrial countries because in low- and middle-income countries, there are insufficient resources. Such techniques are often too cost intensive and there is less responsibility to remediate polluted and abandoned mining and ore processing sites. These examples of remediation techniques are described in more detail in Mulligan et al. (2001). The main challenge for remediation is that there is no cost-efficient remediation technique available to remove the different types of metals and metalloids in one go. This is because their different physicochemical properties and their different distribution patterns in the environment depend on the pH, soil composition, and their different bioavailability. Furthermore, there is no general method that can be used to remediate polluted sites completely. Moreover, before remediation of polluted sites can be undertaken, assessments of surface and groundwater streams and geological formations are required. Once this information is available, it is possible to find the most cost-effective, functional, and efficient methods for removing the hazardous pollutants. According to the laboratory experiments of Mkumbo (2012) in Tanzania, a combination of phytoremediation, using local plants, and solidification/stabilization techniques using buried nodules of the sorbent materials zeolite and autoclaved aerated concrete, seem to be feasible and cost-effective methods. While these can be used in low- and middle-income countries to remove heavy metals, the techniques need to be further improved (Mkumbo, 2012).

Theoretical examples

There are several initiatives that focus on improving the performances of mining companies and promoting more sustainable, environmentally-friendly, and ethically reasonable mining activities. These initiatives include the WSSD, the MMSD project, and the ICMM. Despite these initiatives, the mining sector and its accompanying ore processing and refining industries are causing one of the world's worst pollution problems (Blacksmith Institute and Green Cross, 2012). More viable and feasible incentives are required to push forward the implementation of more environmentally-friendly extraction techniques. They also need to increase the level of support for those mining companies or collectives that are seeking to comply with the local legislation, regardless of whether they are operating at a small or large scale. In addition, it is necessary to provide more education for the employees involved in the mining sector. This is especially the case in low- and middle-income countries, where the workers and the environment are affected the most. Obsolete techniques need to be abolished and more sustainable and effective methods promoted. For instance, the implementation of the FAIRMINED certificate is a first step in encouraging responsible small-scale gold mining activities. Small-scale mining communities can get the FAIRMINED certificate by following the required standards. These include requirements for them to:

- Conduct responsible, formal, and legal mining operations

- Take steps to protect the environment

- Meet strict requirements for labor conditions

- Ensure transparency in the trade of FAIRMINED minerals

- Support socio-economic development though a financial premium on the FAIRMINED products.

The FAIRMINED certificate guarantees that:

- During the production of the different mining products, no child under 15 years has worked for the mining organization and no child under 18 years has worked under hazardous or dangerous conditions

- The employees have used appropriate protective gear and attended health and safety training courses

- The product is traded fairly and that a part of the revenue is used for the social development of their communities or in new, more environmentally-friendly mining practices and technologies, minimizing the use of mercury and cyanide and mitigating the negative impacts on the environment and human health (Low, 2012; Fairmined, 2015).

Programs like this contain good, basic approaches that could be expanded and replicated at the international level and for other mining commodities as well. The implementation of FAIRMINED, FAIRTRADE, and FAIRPRODUCED labeled ores and mining commodities would be helpful in encouraging more responsible mining activities (for small-scale and large-scale operations) provided the requirements of the certificates are well controlled and reliable. With the help of trustworthy and serious certificates, it would be possible for consumers to make their own decisions as to whether they prefer to buy products that are mined and produced under ethically reasonable and more environmentally-friendly conditions. Their alternative would be to buy products where it is unclear whether the miners worked under bad and dangerous conditions, child labor was accepted, small-scale communities were exploited by mercenary authorities, and the environment polluted through using obsolete techniques.

Improvement in the recycling of metals and metalloids

In future, the focus should be on improving the secondary production of metals and metalloids and finding more sound and efficient methods of secondary extraction. This is feasible worldwide (even in low- and middle-income countries) and is better than focusing on expanding primary production. Basically, recycled metals are cheaper. The smelting and refining of scrap uses less energy and is more cost effective than the extraction, smelting, and refining of metals and metalloids from ores. For example, recycling iron saves 20% of the energy used to mine and process the ore. For copper, the comparable saving is 60% and for aluminum it is 90%. In addition, in secondary production it is not necessary to destroy and deforest valuable and vulnerable natural environments. Additionally, there is no disposal or stockpiling of the e-wastes and solid wastes associated with the processing of the ores of heavy metals and metalloids. Thus, compared to primary production, secondary production is more sustainable (Visser, 2012). Although secondary production is more sustainable, at this time, the recycling of metals and metalloid is still quite challenging. And, although in principle, metals are infinitely recyclable, under present conditions, the recycling of metals and metalloids is often inefficient, and not every single metal or metalloid can be recycled efficiently. The widescale blending of different metals and metalloids to enhance their physicochemical properties and their characteristics – their resilience, thermal and electrical conductivity, hardness, and resistance to corrosion – makes the secondary production of metals and metalloids even more difficult (Reck and Graedel, 2012; Visser, 2012). The United Nations Environment Programme (UNEP) and the International Resource Panel indicate that the capability of being recycled varies among the different metals. The estimated global end-of-life recycling rates (EOL-RR) indicate that of 60 metals which are discarded, 18, such as silver, aluminum, gold, cobalt, chromium, copper, iron, manganese, niobium, nickel, lead, palladium, platinum, rhenium, rhodium, tin, titanium, and zinc, are recycled 50% of the time (Graedel et al., 2011a, b). Three metals, iridium, magnesium, and molybdenum are recycled between 25 and 50% of the time (Figure 24). However, these data show that most discarded metals are recycled less than 1% of the time. In addition, in Figure 24, the most hazardous metals and metalloids that are released into the environment through mining activities are highlighted (white boxes).

In general, with the continuously increasing production and use of metals and metalloid-containing commodities (in electronics and construction materials), the inefficient disposal, separation, collection, and storage of metals and metalloids, and their inefficient recycling make it difficult to meet the demand. Therefore, at this time, mining, even though it is less cost efficient, is still necessary in order to provide sufficient minerals, metals, and metalloids; secondary production is not efficient enough to meet resource needs (Visser, 2012). However, improvements in and expansion of the secondary production of metals and metalloids would help to achieve a more sustainable closed-loop materials system. Such a development would reduce the deforestation and destruction of valuable environments and reduce the need to dispose of toxic heavy metals and metalloids. However, it is important that only controlled and sound methods should be used for recycling. Today, evidence of the bad practices in the recycling sector that mainly occur in low- and middle-income countries is well known. In some regions, people rifle through piles of rubbish looking for recyclable heavy metals and metalloids. For example, the inappropriate recycling of lead from lead–acid car batteries using obsolete and hazardous methods poses a high risk to human and environmental health (Blacksmith Institute and Green Cross, 2011, 2013). This topic will be discussed in more detail in the following section addressing electronic industry pollutants (e-waste).

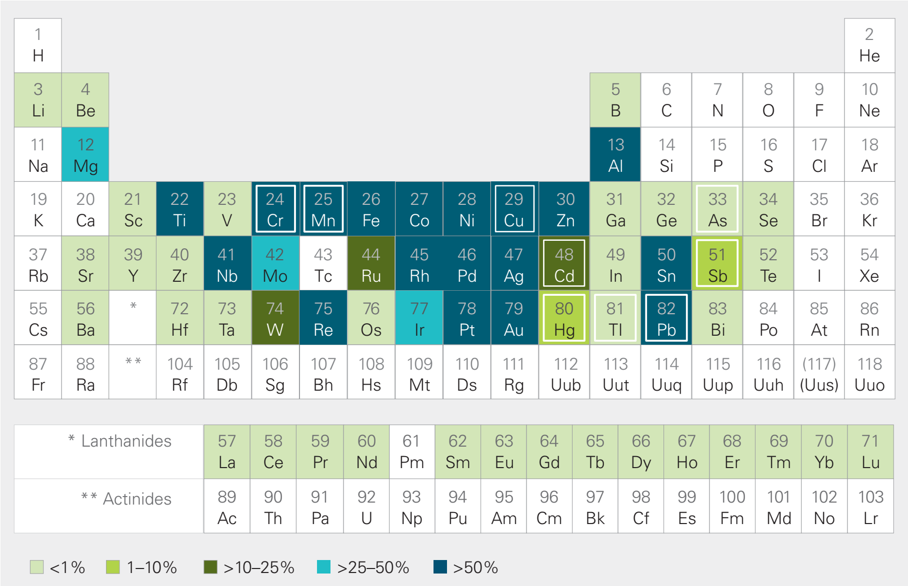

Figure 24: *Global estimates of end-of-life recycling rates for 60 metals and metalloids (Graedel et al., 2011a, b)*