Chapter

Heavy Metals in the Environment and Health Impact

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Abstract

Heavy metals are among the most harmful contaminants in the ecosystems due to their persistency, bioaccumulation and high toxicity. In this chapter, we presented the sources, distribution and pathways of heavy metals in soil, water and air. The physico-chemical properties, uses, toxicity and health hazards of the purely toxic heavy metals lead, cadmium and mercury were also described. Other essential heavy metals were briefly presented and the main health effects due to their deficiency or excess were displayed in this chapter. Finally, the various methods used for the removal of heavy metals from soil and aquatic environments were discussed with a focus on nanomaterials.

Keywords: Heavy metals, classification, properties, uses, health hazards, removal

1. Introduction

Environmental pollution has exposed humans to various contaminants such as pesticides, heavy metals or polycyclic aromatic hydrocarbons [1]. Unlike most organic pollutants, heavy metals are not removed from ecosystems by natural processes. They tend to accumulate in biotic and abiotic environments reaching toxic levels [2–4]. The introduction of heavy metals into the environment can result from natural events as volcanic eruptions, soil erosion and forest fires or anthropogenic activities including mining operations, industrial and domestic effluents and fertilizers application [3].

A number of heavy metals are considered essential for human health. They are important constituents of several key enzymes and play a crucial role in various biochemical reactions [5]. An insufficient supply of these elements leads to various deficiency syndromes. However, these micronutrients can become toxic from a threshold content in the body. Other elements are not beneficial for health and can be highly toxic even at very low levels. This is the case of lead, cadmium and mercury that are among the list of 10 chemicals of major public concern due to their high water solubility, toxicity, and carcinogenesis. Acute and chronic exposure to these elements affects human health and could cause incurable diseases leading to death [2, 3, 6, 7].

2. Classification of metals

Metals are elements with a good electric conductivity and whose electric resistivity is directly proportional to the absolute temperature. Several other physical properties such as high thermal conductivity, reflectivity, malleability and ductility are common to metals [4]. The term "heavy metals" has been widely used in the environmental literature and diverse definitions, based on density, atomic mass or atomic number and on chemical properties, have been proposed for this term [8, 9]. Usually, a heavy metal is an element with an atomic weight between 63.5 and 200.6 and a density greater than 5.0 [10]. Unlike organic contaminants, heavy metals are highly persistent and tend to accumulate in tissues of leaving organisms.

Metals can be classified according to their biological effect. They are considered as "essential" when deficiency symptoms are noted with depletion or removal and "nonessential" when they have no known beneficial role to play in biological function [4]. Essential metals include zinc, copper, iron, iodine, manganese, molybdenum, selenium and vanadium. Lead, cadmium and mercury are among nonessential elements that are highly toxic even at trace amounts. It is important to note that essential elements can become potentially toxic for living organisms if they are incorporated in amounts exceeding a certain threshold [9].

3. Heavy metals in the environment

3.1 Soil

Natural as well as anthropogenic sources of heavy metals including soil erosions, volcanic eruptions, forest fires, mining operations, industrial activities, fertilizers application as well as urban wastes may lead to the contamination of soils [3]. Heavy metals occur naturally in ores in different chemical forms such as sulfides or oxides. Industrial pollution results from various activities such as chemical manufacturing, oil refining, metal processing and plating, tanneries and plastics.

Wind, water and gravity are the principal factors controlling the heavy metals mobility in soils and landscapes. The distribution of metals between solid and solution phases depends on their chemical forms in each phase and on chemical factors such as pH, metal concentration or soil composition. The soil contamination by heavy metals may affect soil fertility by the reduction in populations of soil fauna [3].

3.2 Water

The outbreak of "Minamata disease" and "itai-itai-byo" or "ouch-ouch disease" in Japan during the 1940s and the 1950s drew the worldwide attention to the environmental hazards caused by aquatic heavy metal pollution. Minamata disease was due to the ingestion of fish and shellfish contaminated with highly toxic methylmercury, while ouch-ouch disease was caused by eating rice polluted with lethal amounts of cadmium [1].

Heavy metals enter the aquatic environment from both natural and anthropogenic sources. Entry may be due to direct discharges into both fresh and marine ecosystems or through indirect routes such as dry and wet deposition. Anthropogenic wastes, geochemical structure and mining effluents create potential sources of heavy metals pollution in the aquatic environment.

Once introduced into the aquatic environment, heavy metals are distributed among four interactive compartments (water, suspended matter, sediment and biota). Metals in the aquatic environment can exist in dissolved or particulate form. Sedimentation, adsorption/desorption, dilution and dispersion are the main processes governing the distribution of heavy metals in aqueous ecosystems. Adsorption could be the first step of metals removal from water. Both in marine environments and in fresh water, the permanent or temporary storage of metals takes place in sediments. Microbial activity and oxidative processes can alter the properties of sediments and influence the composition of pore water. Snooping organisms can also bring sediments to the surface, which will release a significant fraction of the metal [11]. The absorption of heavy metals by both fauna and flora could cause an increase in the concentration of the metals in the living organisms. If the evacuation phase is slow, it may result in a phenomenon of bioaccumulation, which could contaminate the aquatic food chain [11].

Unlike biosorption, bioaccumulation is an active process, whereby metals are integrated in the interior of cells [12]. Certain metals bind preferentially, either transiently or permanently, to the cell membrane and then cause structural and functional modifications, which are often fatal to the cell. A study by Dao and Beardall showed that increasing doses of lead administered to the algae *Chlorella sp.* were associated with a decrease in algal growth, as well as an inhibition of the photosynthetic function by the algae [13].

3.3 Air

Heavy metals occur in the atmosphere mainly in particulate form. Particulate matter refers to a mixture of solid and liquid particles that are dispersed in the air. It is composed of primary particles that are emitted directly into the atmosphere and secondary particulates formed through chemical transformation of gaseous pollutants [1]. Metals in the atmosphere result from natural processes (volcanic eruption, soil erosion, sand storms, dust re-suspension) and anthropogenic sources (mainly industrial, agricultural and vehicle emissions). Metal oxides constitute a major class of inorganic particles in the atmosphere. They result from the combustion of fuels containing metals.

Generally, the concentrations of atmospheric heavy metals are higher in winter than in summer. This is probably due to the high temperature, the strong diffusion capacity and the rainfall in summer season. Inversely, the atmospheric deposition of heavy metals tend to be higher in summer than in winter. According to Duan and Tan, the average atmospheric concentration of lead in China is 261.0 ± 275.7 ng m^{-3}, which falls below the guideline limit of the World Health Organization (WHO) of 500 ng m^{-3} [14]. The mean concentration of atmospheric cadmium in the same area is 12.9 ± 19.6 ng m^{-3}, which exceeds the WHO limit of 5 ng m^{-3}. The principal sources of atmospheric heavy metal pollution in China are coal burning, iron and steel industry and vehicle emissions [14].

4. Health impact of heavy metals

4.1 Lead

4.1.1 Physico-chemical properties

Lead (Pb) is one of the oldest heavy metals used in the past for hair dies, insecticides, and pottery glazes [15]. It is a naturally occurring bluish-gray metal, highly malleable and ductile and shiny when just cut. Lead is a dense metal, with a specific gravity of 11.35 and an atomic weight of 207.2 g mol^{-1}. It is present in many inorganic forms (acetates, nitrates, carbonates, sulphates and chlorides) especially in the earth's crust and ores [5]. Lead is also found in the environment as a result of radioactive decompositions because it is a natural product of the decay of uranium. Native lead is rare, it is currently extracted from ore associated with zinc (blende), silver and copper. The main mineral source of lead is galena (PbS) [5].

4.1.2 Uses

Despite its high toxicity, lead is still used in various anthropogenic activities such as storage batteries, fossil fuel combustion, PVC production, electricity generation, alloys, glass manufacture and nuclear industry. Due to environmental pressure, lead emissions from motor vehicle gasoline have decreased significantly over the last three decades. As a result, a great improvement in air quality was observed worldwide [1, 5]. In addition, the use of lead in paints and colorants was banned in most countries after children's intoxications from lead-based pigments.

4.1.3 Health hazards

The main routes of lead exposure include ingestion of contaminated food and drinking water as well as incidental ingestion of dust and soil. Another major exposure pathway is the lead-based paint in older homes. Once inside the body, lead is distributed in blood and soft tissues and accumulated in skeletal bones [1].

One of the major mechanisms of lead toxicity is its ability to interact with proteins and to inhibit enzyme activity by competing with essential metallic cations for binding sites [2, 16, 17]. Acute toxicity can cause fatigue, irritability, sleeplessness, headache, loss of appetite, dullness, hypertension and vertigo, while chronic toxicity can result in neurological disorders, cognitive impairments, premature birth, brain injury, kidney dysfunctions, reproductive pathologies, liver damage, paralysis and even death [16, 18, 19]. Lead poisoning affects particularly children leading to hyperactivity, behavioral problems, lowered intelligence quotient (IQ) and cognitive deficits [20]. In Chicago, after adjustment for all socio-demographic factors, it was reported that exposure to lead caused 13% of reading failure and 14.8% of math failure in children [21]. Adverse effects of lead toxicity are also found in contaminated ecosystems, including biodiversity losses, decreased growth in plants and animals and neurological damages in vertebrates [22].

4.2 Cadmium

4.2.1 Physico-chemical properties

Cadmium (Cd) is a soft, bluish-white metal with an atomic weight of 112.4 g mol^{-1} and a density of 8.65. It melts at 594 K. Cadmium was first discovered by Friedrich Stromeyer in Germany in 1817. It is a rare element that is not found as a pure state in nature and is commonly associated with zinc (one ton of zinc provides about 2.5–3 kg of cadmium. Cadmium is also present in lead and copper ores, as well as in natural phosphates (40 ppm for Tunisian phosphates, 26 ppm for Moroccan phosphates). In the latter case, various decadmination processes can be implemented [23]. Cadmium persists in the environment and has a biological half-life of 10 to 25 years [1].

4.2.2 Uses

Cadmium is used in various industrial processes including electronics, electricity, metallurgy, plastics, PVC manufacture, pigments and paints and pesticides [1, 24]. Significant quantities of cadmium are also found in discharges from industries processing crude phosphate [23]. Due to environmental restrictions, the use of cadmium in the manufacturing of nickel-cadmium batteries decreased and has been replaced by nickel-metal hydride and lithium-ion batteries. Recently, cadmium telluride was used in semiconducting solar panels and infrared optical windows [25].

4.2.3 Health hazards

Dietary intake is the most important pathway for cadmium exposure in humans. Tobacco smoke is another source of exposure containing appreciable amounts of the metal. As the absorption of cadmium from the lungs is much higher than from the gastrointestinal tract, smoking contributes significantly to the total body burden [1]. Cadmium is absorbed in the gut and the lungs, and transported to the liver by blood. Accumulation of cadmium in the body is done mainly in the liver and the kidneys [18]. Cadmium metallothionein is the form in which cadmium enters the kidneys. This complex has a protective role against cadmium toxicity through binding up to seven metal atoms per molecule. When the cadmium intake is too high, the metal is transported further to the kidneys and binds to other proteins [5, 17].

Adverse effects of cadmium toxicity include high blood pressure, reproductive disorders, fetal growth reduction, pregnancy loss, iron deficiency, gastrointestinal disorders, bone fracture, nephrotoxicity, renal dysfunction, neurological troubles, lung damage and lung cancer [1, 18, 24, 26]. In humans, blood, urine, hair and nails have been used as biomarkers of cadmium exposure and health risk evaluation [27]. Recently, Du et al. (2020) evaluated the environmental and human health hazards from cadmium exposure near an active lead-zinc mine and a copper smelter in China. They found that the cadmium concentration in hair and urine biomarkers in the mining and smelting areas were much higher than in the general population. Additionally, rice and vegetable ingestion were the two major pathways of cadmium exposure [28].

4.3 Mercury

4.3.1 Physico-chemical properties

Mercury (Hg) is a heavy metal with a density of 13.6 and an atomic weight of 200.6 g mol^{-1}. It is rare in the earth's crust and occurs in several forms of ore. *Cinnabar* HgS is the principal mercurial mineral [1, 5]. Mercury is a unique metal, as it is the only metal liquid at room temperature. In addition, it exists in nature in three forms (elemental, inorganic, and organic). In the atmosphere, most mercury is present in the form of elemental mercury vapor, while inorganic and organic species predominate in soil, water, plants and animals. Methylmercury, an organic compound of mercury, is formed as a result of the methylation of inorganic forms of mercury by microorganisms in soil and water [29].

4.3.2 Uses

Mercury is extensively used in various industries such as the production of caustic soda, the wood processing, the pulp and paper industry or the manufacture of batteries. Mercury is also employed as preservative of pharmaceutical products, as amalgams in dental industry, or as catalysts in chemical industry. Due to the linearity of its coefficient of expansion, mercury is used as a metal in thermometers. In addition, mercury is used in jewelry making, pesticides, barometers and incandescent lights [1, 5, 16, 30].

4.3.3 Health hazards

Fish consumption and dental amalgam are the major sources of mercury exposure in humans. Inhalation of mercury vapor is an other important pathway of exposure. Due to their high lipophilicity, elemental mercury and methylmercury are highly absorbed in the tissues. Inorganic mercury salts are not lipid soluble; therefore, they do not cross the placental and blood–brain barriers. Absorption of methylmercury from the gastrointestinal tract in humans exceeds 90%, whereas absorption of inorganic mercury salts is less than 10% [7]. Once absorbed in the body, the inhaled mercury vapor is quickly diffused into the blood and distributed into all of the organs [6]. Then it is accumulated in the brain and the kidney and excreted through urine and feces. As regards methylmercury, this organic compound is accumulated in the liver and kidney after consumption and slowly converted to inorganic mercury by microflora in the intestines [31].

The toxicity of mercury, especially methylmercury, derives from its ability to interact with nucleophiles due to its electrophilic nature. During interactions, the catalytic, binding, and transport functions of nucleophiles are impaired. One essential mechanism related to the toxicity of mercury is the damage to mitochondria that enhances the generation of free radicals [17]. The major clinical features of mercury acute and chronic exposures are insomnia, weight loss, vomiting, diarrhea, cough, dyspnea, fever, tremors, gingivitis, erythrism, delusions, hallucinations, acrodynia disease, congenital malformation, renal tubular dysfunction, neurologic disorders, paralysis and death [17, 32].

4.4 Other essential metals

Most essential metals act as catalysts for enzymes and can become toxic at high levels. In tissues and fluids, metals very often form complexes with organic compounds such as amino acids, proteins and peptides. **Table 1** displays the main health effects due to deficiency or excess of five essential metals (iron, zinc, copper, iodine and selenium) [33–38].

4.4.1 Iron

Iron (Fe) is a vital nutrient as it is a cofactor of a wide variety of cell functions. In the human body, iron is found as heme compounds (hemoglobin or myoglobin), heme enzymes, or nonheme compounds (flavin-iron enzymes, transferring, and ferritin). The body requires iron for oxygen transport, respiration, the tricarboxylic acid cycle, lipid metabolism, gene regulation and DNA synthesis [39, 40]. Inorganic iron and heme iron are the two forms of dietary iron. Good sources of heme iron include meat, poultry and fish whereas nonheme iron is obtained from cereals, pulses, legumes, fruits and vegetables. Iron absorption is enhanced by vitamin C, ascorbic acid and meat consumption, while phytates, calcium and some dietary fibres inhibit the nutrient absorption [41, 42].

4.4.2 Zinc

Zinc (Zn) is an essential nutrient found in all human tissue. It is a structural compound of nearly 300 enzymes, important for the metabolism of macromolecules and that of nucleic acids. It has been estimated that the adult human body contains approximately 2 g of zinc. Lean red meat is an important dietary source of zinc. In addition, its zinc is present in a highly available form. However, fats, oils, sugar and alcohol have a very low zinc level [34, 43].

4.4.3 Copper

Copper (Cu) is essential for the activity of several metalloproteins and enzymes. It plays a crucial role in the regulation of the gene expression. Copper is required for

Metal	Deficiency health effects	Toxicity health effects
Iron	• Anemia • Mental retardation • Brain damage • Behavioral impairment	• Liver and heart disease • Cancer • Neurodegenerative disorders • Diabetes • Hormonal abnormalities
Zinc	• Diarrhea • Growth retardation • Behavioral changes • Defects in the immune systems • *Acrodermatitis enteropathica* genetic disorder	• Nausea and vomiting • Diarrhea • Fever • Lethargy • Anemia • Copper deficiency
Copper	• Hypochromic anemia • Neutropenia • hypopigmentation • Osteoporosis • Vascular abnormalities • Neurologic disorders	• Wilson's disease • Hepatocellular degeneration • Necrosis • Brain damage • Death
Iodine	• Goiter • Congenital anomalies • Cretinism • Hypothyroidism • lmpaired mental function • Hyperthyroidism	• Goiter • Hypothyroidism • Hyperhyroidism
Selenium	• Keshan disease • Kashin-Beck disease	• Gastrointestinal disturbances • Hair loss • Nail brittleness • Skin rash • Garlic breath odor • Fatigue • Irritability • Neurologic disorders

Table 1.
Main health effects of deficiency and excess of essential heavy metals.

growth, defense, strength, blood cell production, iron transport and metabolism. The total body content of copper has been estimated to be 80 mg, with a range of 50–120 mg. Dietary sources rich in copper include seafood, organ meats, legumes and nuts. Refined cereals, sugar and dairy products are poor in the nutrient [35, 44].

4.4.4 Iodine

Iodine (I) is needed for the synthesis of thyroid hormones which are involved in the growth, development and control of metabolic processes. Deficiency of iodine during early development of the brain and nervous system leads to cretinism, which is irreversible. At an older age, it leads to hypothyroidism and goiter, the first endemic disease that has been attributed to environmental factors. Marine fish and shellfish are foods particularly rich in iodine [37, 45].

4.4.5 Selenium

Selenium (Se) is a component of the amino acid selenocysteine. Enzymes that depend on selenium play a very important role in cells. They offer protection against oxidative damage, modulation of growth and development as well as defense against infection. In humans, selenium deficiency can cause endemic cardiomyopathy known as "Keshan disease", which mainly affects children and women of childbearing age. Liver, kidney and seafood are particularly rich in selenium [36, 46].

5. Removal of hazardous heavy metals

5.1 Methods of treatment

Due to their toxicity, non-biodegradability and persistency, heavy metals can exert adverse effects on the environment and other ecological receptors. Therefore, their removal from soil and aqueous environments has drawn tremendous attention. Various methods have been developed and used to decrease heavy metals concentrations in the ecosystems. These technologies can be categorized in physico-chemical processes such as ion exchange, reverse osmosis, membrane filtration, adsorption, precipitation, electrolytic removal and biological processes involving activated sludge and phytoremediation [12, 47, 48]. Adsorption is one of the most extensively used methods due to its low cost and simple preparation. It is based on mass transfer between the liquid phase and the solid phase called adsorbent. This process can run in reversible mode and the adsorbents will be regenerated by desorption. Some widely used adsorbents for removal of metal ions include clay minerals, activated carbon,, biomaterials, industrial solid wastes and zeolites [48]. Low cost adsorbents include natural material or certain waste from industrial or agricultural operation.

5.2 Nanomaterials for heavy metals removal

Over the past decades, nanomaterials have gained a lot of attention due to their high specific surface area, catalytic potential and chemical reactivity [49]. Various cost-effective and safe nanomaterials have been developed in treating wastewater solutions. Among them, nano metal oxides (NMO), nano zero-valent iron (nZVI) and hybrid magnetic nanoparticles (MNP) are particularly efficient in the improvement of water quality.

5.2.1 Nano metal oxides

Metal based nanomaterials are commonly oxides of iron, manganese, titanium, magnesium, copper and cerium. These metal oxides are low-cost materials and provide a high adsorption capacity and selectivity. However, NMO are prone to agglomeration due to their poor stability. Different techniques could be used for NMO synthesis such as hydrothermal techniques, chemical co-precipitation, thermal decomposition or chemical vapor condensation [50, 51]. Generally, highly stable, monodisperse and shape-controlled NMO are the result of efficient synthetic techniques. Luther et al. (2012) synthetized iron oxides nanoparticles for the removal of arsenic (III) or (V) from aqueous solutions. The adsorption followed the Langmuir Isotherm and capacities were determined for each nanomaterial and arsenic ions [52]. Optimum binding capacities reaching 20000 μg/g for arsenic (III) and 4904 μg/g for arsenic (V) were observed at pH =6, after 24 h of contact time at room temperature.

5.2.2 Nano zero-valent iron

Due to the reducing capacity of iron (0) and the high reactivity of ferric oxide, nZVI composite was extensively investigated as a novel adsorbent to remove heavy metals from wastewater [53]. Several methods have been developed to produce nZVI including abrasion, grinding, reduction with sodium borohydride, carbothermal reduction, ultrasound assisted method, electrolysis or biosynthesis [54]. In spite of their effectiveness in water treatment and remediation, some disadvantages mainly due to aggregation, difficult separation and lack of stability are encountered with the use of nZVI. To overcome these technical difficulties, modifications of nZVI could be applied such as doping the composite with noble metals, surface coating with polymers or anionic surfactants, emulsification or immobilization with silica, activated carbons or zeolites. Huang et al. (2015) applied modified nZVI with sodium dodecyl sulfate anionic surfactant for chromium (VI) removal [55]. They found an enhanced removal capacity and a great stability with nZVI modification. The adsorption followed the pseudo-second order kinetic model and the Freundlich Isotherm. The highest removal efficiency of chromium (VI) was obtained at pH 3.0 and 25°C, at the value of 98.919% after 120 min of contact time.

5.2.3 Hybrid magnetic nanoparticles

Hybrid magnetic nanostructures contain two or more nanometer-scale components with at least one component being magnetic [56]. These hybrid nanocomposites take the advantages of the magnetic nanoparticles such as their high surface area, their easy separation under external magnetic fields and their excellent recyclability after separation and prevent from their precipitation or aggregation due to their tendency to oxidation [57]. Up to date, different MNP have been researched by the scientific society. The investigated nanostructures include magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3). They could be functionalized with different materials such as polymers, biomolecules, inorganics, organics or carbon nanotubes [57]. This surface functionalization improves the homogeneity, selectivity and adsorption capacity of magnetic nanoparticles leading to an effective removal of toxic pollutants. Asadi et al. (2020) synthetized the spinel ferrites nanoparticles $MnFe_2O_4$ and $CoFe_2O_4$ to investigate the zinc removal from aqueous solution. High respective adsorption capacities of 454.5 and 384.6 mg/g for $MnFe_2O_4$ and $CoFe_2O_4$ were obtained at optimum pH =6, by following the Langmuir Isotherm model [58].

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