Chapter

Environmental Impacts of Heavy Metals and Their Bioremediation

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Abstract

Fast consumption, increasing energy needs, unplanned urbanization, and unconscious discharge of industrial wastes cause pollution of air, soil, food and water resources. Among these pollutants, heavy metals and metalloids are not biodegradable and accumulate in compartments such as water, soil and plants, threatening human and environmental health. Monitoring studies show that heavy metals such as arsenic, lead, mercury, cadmium, nickel, zinc, copper, chromium and trace elements are in first place according to their availability in the environment. Preventive and remedial measures should be taken to reduce the effects of heavy metals. Legal regulations, monitoring studies, the use of soluble and non-toxic compounds in environmental compartments (air, water, soil and plants) in industrial processes, heavy metal-free pesticides, appropriate wastewater treatment plants and use of renewable energy sources instead of fossil fuels are among the priority measures to reduce concentrations of heavy metals in the environment. As a bioremediation approach, removing toxic wastes from the environment by using bioaccumulatory organisms such as plants or mussels maintains its importance among studies aimed at recovery. Studies have shown that integrated methods - especially the combination of suitable plants and microorganisms - are very effective in mitigating the effect of heavy metals in the environment.

Keywords: heavy metal, environmental matrix, mitigation, human health, ecosystem health, bioremediation

1. Introduction

While the 21st century offers many technological possibilities to the service of humanity, humans try to dominate nature by using science and technological facilities and change the existing balance. The deteriorating natural balance and environmental problems that occur as a result are the most important hazards that threaten health in our age. The effects of climate change increase in parallel with increasing environmental problems. With industrialization, mining, pesticide use and increasing energy needs, heavy metals come to the forefront primarily in relation to occupational diseases, and they are also among the pollutants that disrupt the ecological balance as a result of water, soil and air pollution. Under normal conditions, the proportion of heavy metals in nature is low. When the concentration ratio in the natural environment increases, heavy metals such as arsenic, mercury, cadmium, chromium and lead have toxic effects, especially on organisms, and inhibit enzymes. They create environmentally toxic effects with their non-degradable and accumulatory properties in environmental compartments [1–3]. While some metals are important as trace elements for living organisms, they may accumulate in living organisms above a certain concentration and cause toxic effects or they can convert to other compounds in the environment; during this transformation, toxic and water-soluble compounds of a metal may sometimes occur. For this reason, heavy metals and trace elements are classified as vital and non-vital according to their degree of participation in biological processes. Those defined as vital must be present at a certain concentration in the structure of the organism. Because these metals participate in biological reactions, they must be consumed regularly in foods. For example, copper is an indispensable element in red blood cells and in many oxidation and reduction processes in animals and humans. On the other hand, non-vital heavy metals can cause health problems by affecting the physiological structure even at very small concentrations. The best example of this group is mercury, which binds to sulfurous enzymes. Whether a heavy metal is necessary for living organisms depends on the organism being considered. For example, while nickel is toxic to plants, it must be present as a trace element in animals [4–6].

2. Heavy metals and their impacts

There are more than 32 metals in the periodic table. Heavy metals are metals with high density and toxic effects even at very low concentrations, with a density of 5 g/cm^3 or higher [7]. These metals enter water, nutrients, soil and air ecosystems from the earth through natural processes and through anthropogenic activities [8]. These are considered major pollutants because of their toxic effects on living organisms and their prevalence in the world. Al, Fe, Cr, Sb, As, Be, Cd, Cu, Pb, Hg, Ni, Se, Ag and Zn are classified as primary contaminant metals by the United States Environmental Protection Agency (US EPA) [9]. In addition, the Agency for Toxic Substances and Disease Registry (ATSDR) has included heavy metals on the priority chemicals list due to their potential threat to human health and their toxicity [10].

2.1 Arsenic and arsenic compounds

Inorganic arsenic (As) is a gray-colored element with a molecular weight of 74.92 g/mol found naturally in the earth's crust. However, inorganic arsenic often coexists with other elements such as oxygen, chlorine, and sulfur. Inorganic arsenic compounds include arsenic pentoxide, arsenic trioxide, and arsenic acid. The combination of carbon and hydrogen with arsenic creates organic arsenic. Organic arsenic compounds include arsanilic acid, arsenobetaine and dimethylarsinic acid. Pure arsenic is rarely found in nature and is not very toxic, but it can be oxidized easily in humid air and become toxic by conversion to arsenic anhydride. Arsenic, which has four different oxidation steps, is mostly in the form of +3 and + 5 valences in nature [1, 11, 12].

There are many uses of arsenic compounds in industry. Arsenic acid (AsO4H3), arsenic trichloride (AsCl3), arsenic triiodide (AsI3), arsenic anhydride (As2O5), copper arsenide ([Cu3 (AsO3) 2) and very toxic compounds such as calcium arsenide [Ca3 (AsO4)5], lead arsenide [Pb3AsO4) and sodium arsenate (Na2HAsO4), which are highly water soluble, are used for the production of paint (green, yellow), glass, ceramics, and semiconductors. Arsenic compounds can also be used as insecticides. Sodium arsenate (Na2HAsO4, 7H2O) is used to kill some parasites in viticulture, fruit cultivation and potato growing. Arsenic compounds have also been used as chemical weapons. Lewisite containing arsenic is a volatile liquid (chlorovinyldichloroarsine) and Adamsite (diphenylaminechlorarsine) is a solid substance used in the form of aerosol. These substances have vesicant, irritant and sternutatory properties. Arsenious anhydride or arsenic trioxide (As2O3) is one of the most toxic compounds among arsenic compounds. It is a white powder, dissolves quickly in alkalis, acids and hot water, and contains arsenous acid (H3AsO3). Since it is volatile, it easily enters through the lungs, but there is a risk of loss during toxicological searches. As2O3 was used as a rat poison since medieval times. Today, arsenic compounds are used in limited amounts (10%) as rodenticide. Arsine (AsH3), or arsenous hydrogen, is a colorless gas with an unpleasant garlic odor. It is released as a result of contact between inorganic arsenic compounds with hydrogen or the hydrolysis of metallic (zinc, aluminum, etc.) arsenides with water or an acid, especially during washing of some metal parts with acids (H2SO4). Ethyl arsine is formed by the interaction of various fungi with arsenic compounds. The toxicity of arsenic compounds generally depends on their solubility in water: Pure metal arsenic and inorganic compounds (sulfides) are insoluble in water and theoretically lack toxic effects, though in a humid environment, they can be oxidized to toxic compounds (As2O3). Water soluble inorganic compounds (arsenous anhydride, arsenide, alkaline arsenates) are very toxic; and arsenic hydrogen or arsine (AsH3) has a different toxicity than other forms of inorganic arsenic as a hemolytic poison. There is a reaction with thiol groups. Mold and dampness increase the toxicity of arsenic compounds. Organic arsenic compounds have lower toxicity, they are eliminated faster from organisms [1, 13–15].

Arsenic compounds block the thiol (-SH) groups of many enzymes that play a role in cell respiration and different metabolisms in organisms. By inhibiting the oxidative decarboxylation of pyruvic acid, they disrupt the metabolism of carbohydrates, lipids and amino acids and form a true "biochemical lesion". Since the skin and keratinized tissues are rich in sulfur, the accumulation of arsenic compounds here is directly related to their attraction to thiol groups [1]. The International Agency for Research on Cancer (IRAC) has classified inorganic arsenic as a Group 1 carcinogenic to humans [16]. The Environmental Protection Agency (EPA), on the other hand, classified it as a Group A human carcinogen. The EPA calculated the cancer slope factor for inorganic arsenic oral exposure as 1.5 mg/kg/day. No cancer inhalation studies are available in humans or animals for arsine. The EPA has not classified arsine for carcinogenicity. The EPA set limits on the amount of arsenic that can be released into the environment from industrial sources. For this, the amount of arsenic permitted in drinking water was determined as 0.01 ppm [17].

2.2 Lead and lead compounds

Lead and its derivatives are industrial toxic substances that have been widely used by humans for centuries and therefore play an important role in environmental pollution. Lead is a metal found in nature. It is a bluish gray metal that is rarely found in the earth's crust. It occurs mainly as lead ore, and the most important ore is lead sulfide (galena). It is found in a variety of compounds such as lead, lead acetate, lead chloride, lead chromate, lead nitrate, and lead oxide. While pure lead is insoluble in water, the solubility of lead compounds in water varies. The chemical symbol of lead is Pb and its atomic weight is 207.2 g/mol. Its vapor pressure is 1.77 mm Hg at 1000°C [18]. In nature, pure metal or its oxides, inorganic salts such as carbonate, sulfate, nitrate and acetate, and organic compounds such as lead tetraethyl exist. The primary use of lead is in the manufacture of batteries. In addition, it is widely used in in the production of paint, alloys and metal products (lead-antimony and lead-tin) in industry, electronic conductors, rubber, sheet lead, waterproof plates (roofing) or sound and radiation insulation, linoleum, solder, pipes, ammunition and toys. Its use for ceramic glazes, paint and pipe soldering has decreased significantly. In addition, it is used in the composition of some ointments (lead acetate), diluted lead acetate (as abortive) is used infrequently in treatment under the name white water and as an insecticide (lead arsenate) in agriculture. Tetraethyl lead was used as a gasoline additive to increase the octane rating, before the EPA banned its use in gasoline in 1996 in the USA. Leaded gasoline is still used for propeller planes and some race cars [1, 19]. Metallic lead is a bluish, gray-silver soft metal. It melts at 327°C, is quite dense and can easily stretch (can take the form of a wire). It is not affected by dilute hydrochloric acid and sulfuric acid. It forms concentrated sulfuric acid and hot lead sulfate. Lead melts even in cold temperatures, forming lead nitrate and nitrous vapors. Organic acids (acetic acid, citric acid, etc.) affect lead slowly and cause the formation of their respective salts. It emits steam at temperatures above 500°C and harmful metallic dust. Lead is slightly soluble in water and may be the source of toxicity in some drinking water. Lead oxides usually form from water-insoluble compounds. PbO “oxide” (yellow masikot) forms yellow-orange lead oxide (lilac) when heated and is used for glass, enamel, accumulators, etc. in industry. PbO2 “bioxide” is the red oxide of lead and is an energetic oxidizer. Pb3O4 “minium” (cinnabar, plombi orthoplumbus) is a red-colored compound added to antirust paints and used in the varnish, enamel, crystal and battery industries. It is formed by heating lead oxide in air flow at 500°C. Lead sulfide is the substance that forms the mineral galena in its natural state. It is insoluble in water. It is found in the combination of yellow-colored varnishes used in ceramics and pottery, and color changes to dark brown when manganese oxide is added or green when copper oxide is added. These varnishes continue to be used in many countries today. It can be dissolved with organic acids. Food or acidic liquids (vinegar, wine, lemon juice, etc.) should not be placed in containers painted with this type of varnish. Lead hydrocarbonate is mixed with linen oil and used to obtain white paint. However, these dyes darken with the effect of hydrogen sulfide in the air and also have toxic effects. Although its use is prohibited in many countries, residues in old settlements can cause some poisoning cases. Arsenate lead was formerly used as insecticide in agriculture, including in Turkey, before being banned in many countries because of its toxicity. However, some residues from past use can be found in the soil due to its durability. Lead chromate is also called “chrome yellow” and can be used to obtain yellow dye. Lead stearate is used to reinforce some plastic materials. The basic iodide and acetate of lead -lead iodide and lead acetate (soluble in water)- are used in dermatology to benefit from solubilizing effect in the form of a solution. Basic lead acetate is a compound made by neutralizing lead acetate with lead oxide (PbO). Lead naphthenate is used as an additive in some moisturizing drugs. Alcoholic derivatives of tetraethyl-lead and tetramethyl-lead are organic derivatives of lead that are added to gasoline as an antidetonante (0.5%). Often ethylene dibromide and ethylene dichloride compounds are added to engines to prevent metallic lead build-up. Exhaust fumes from cars operating with leaded gasoline contain lead halides and oxides as well as a small amount of undissolved lead-alcohol (1–10%). In many countries, the proportion of lead in gasoline is legally limited (0.5 g/l) and unleaded gasoline vehicles are now produced. These organic lead derivatives added to gasoline play an important role in air pollution (especially in big cities) [1, 20].

Lead is taken into the organism generally through digestion (in the form of food, liquid drinks, vapor or particles) and through the respiratory tract. It is a highly toxic metal that enters biological systems by mixing with respired air and nutrients from the air, water and soil. Up to 90% of the lead in the atmosphere in solid and gaseous form is absorbed by the lungs. Small lead dust or vapor, especially in the air, cause lead compounds (oxides or salts) to enter the organism by inhalation. Very small particles can reach the alveoli, while large particles are discharged from the upper respiratory tract or can be reabsorbed by entering the digestive tract through sputum and saliva. When organic lead compounds contaminate the skin, they can be absorbed significantly, especially from lesioned areas. When the carcinogenic effect is examined, human studies are insufficient regarding lead exposure and increased cancer risk. In animal studies, kidney tumors were reported in rats and mice orally exposed to lead. Lead is assessed as B2 (possible human carcinogen - based on evidence of adequate carcinogenicity in animals) according to the Guidelines for Carcinogenic Risk Assessment (US EPA, 1986) [1, 21].

2.3 Mercury and mercury compounds

Elemental mercury (Hg) is a silver-white metal with an atomic weight of 200.59 g/mol. Mercury is liquid at room temperature and has a vapor pressure of 0.002 mm Hg at 25°C. Mercury can be found in three oxidation states; elemental-metallic (Hg), precious mercury-mercurous (Hg +) and divalent mercury-mercuric (Hg ++), as well as both inorganic and organic compounds. Inorganic mercury compounds include mercury chloride, and mercury sulfide. Organic mercury compounds include mercuric acetate, methylmercuric chloride, dimethyl mercury, and phenylmercuric acetate. These different forms transform into each other in the natural environment (for example, methylation of inorganic Hg, oxidation of metallic mercury to inorganic compounds, etc.). All types of mercury are highly toxic, and the toxic properties of these different mercury compounds are quite different: inorganic and organic mercury differ from each other in terms of entry and absorption routes [1]. Mercury is one of the main elements involved in the formation of the earth's crust. Mercury, which is generally found in superficial layers, is used in many areas today. However, its usage areas are narrowing due to the risk it creates. Mercury (Hg) compounds are used in industry, paint, explosives, electronic devices, accumulators, thermometers, etc. It is used in construction. The main source of mercury contamination in the world is the production of alkali chlorine to obtain electrolytes from chlorine and sodium hydroxide in industry [1, 22].

Elementary mercury (metallic mercury) is a very dense liquid and volatile at ambient temperature. A major source of exposure for elemental mercury occurs via inhalation in occupational settings. Elemental mercury is used in thermometers, barometers and pressure-sensing devices. It is also used in batteries, lamps, industrial processes, and in oils used for purification and lubrication. Another source of exposure to low levels of elemental mercury in the general population is elemental mercury released from amalgam fillings in teeth. It is generally taken into the body in the form of steam. Mercury vapors readily cross the alveolar barrier. Inorganic mineral mercury salts can be mono or divalent (mono- or divalent). Today, the general population is not exposed to significant inorganic mercury compounds. Most products containing these compounds are now banned. Until 1990, mercury compounds were used in latex paint to prevent bacterial and fungal growth. The EPA banned all interior paints containing mercury in 1990, and exterior use after 1991. Although agricultural and pharmaceutical use of inorganic mercury has ceased in the United States, mercury chloride is still used as a disinfectant and pesticide. Mercury chloride (bivalent), also known as sublimation, has a corrosive (caustic, burning) effect. Inorganic mercury (mono) salts, such as calomel, are less soluble than divalent compounds and show lower toxicity. After exposure to inorganic mercury salts, the main storage locations are kidney and brain tissue. Organic mercury compounds are in the form of alkyl or aryl derivatives. Methyl-Hg (methyl mercury) is the most important of these compounds in terms of toxicity. Methyl mercury has no industrial use; it forms by methylation of inorganic mercury ions in the environment. Methyl mercury exposure mostly occurs through diet, especially fish and fish products. In the past, sources of methyl mercury exposure included fungicide-treated cereals and meats from animals fed such cereals. However, fungicides containing mercury are banned in the USA today and exposure through this route does not occur at present [1, 23].

Mercury is listed as a contaminant of concern by the EPA due to its persistence in the environment, its bioaccumulative potential, and its toxicity to humans and the environment. In today's world where environmental health conditions are decreasing, people are constantly exposed to metal (elements) and organic mercury compounds. Contamination of the environment with mercury as a result of distorted industrialization, use of mercury in fossil sourced petroleum products, fungicides, chemical production, used batteries, use in hospitals and use against mold cause intense exposure of humans and foods (fish, plants, etc.) to mercury. Significant amounts of mercury come from the atmosphere with annual rainwater. Pollution with mercury is more common in closed seas and inland waters than in open seas. For this reason, mercury accumulation occurs more rapidly in creatures living in contaminated waters. Mercury is found in the water system in elemental, inorganic and organic forms. Organic mercury in water is found either in the form of covalently-bonded organic mercury (methyl mercury) and dimethyl mercury (less toxic than methylmercuride) or mercury complexed with organic matter (humic substances). Methyl mercury is a metabolized form of mercury and is highly toxic to human embryos and fetuses. It is shaped by the effect of microorganisms in fish and accumulates to a degree that threatens human and animal health. Especially large fish (predators) that feed on small fish pose a problem in this regard. High levels of methyl mercury can be obtained from fish that are fed or caught in contaminated areas [1, 24]. Between 1953 and 1956, a type of mercury poisoning called "Minamata disease" occurred in Japanese fishermen. It was understood that these fishermen had eaten fish they caught in waters contaminated with organic mercury wastes from a factory producing plastic in the vicinity for a long time [25]. The use of organic mercury compounds in agriculture poses a risk in terms of environmental and food pollution [26, 27].

Various studies were conducted on elemental mercury and cancer in humans. However, the EPA classified elemental mercury as group D, which cannot be classified as a human carcinogenic, based on insufficient human and animal data. There are no studies on the carcinogenic effects of inorganic mercury in humans. The EPA classified inorganic mercury compounds in the possible human carcinogen group C, as there is insufficient data in humans and animals. There are no studies on the carcinogenic effects of methyl mercury in humans. Based on insufficient data in humans and limited evidence of carcinogenicity in animals, the EPA classified it in group C as a possible human carcinogen [28].

2.4 Cadmium and cadmium compounds

Cadmium is a soft silver-white metal often found in combination with other elements. Although cadmium compounds are not normally soluble, their solubility in water is quite good. The chemical symbol of cadmium is Cd and its atomic weight is 112.41 g/mol. Cadmium is found in nature in the form of yellow cadmium sulfide (CdS), together with zinc ore [29]. Cadmium, one of the most dangerous heavy metal pollutants in the ecosystem, is a toxic metal discovered by Friedrich Stromeyer in 1817. The industrial use of cadmium goes back 50 years. Due to its noncorrosive features, it is widely used in the aircraft industry, as a neutron absorber in nuclear power plants, as a stabilizer in insecticide formulations, plastic production, and in the paint and nickel cadmium battery industry. It occurs as a by-product in lead production. This situation is significant in terms of environmental pollution. Cadmium contaminates water and soil by transfer into soil and water from industrial waste and residues. Due to the long-term use of phosphorus fertilizer and treatment sludge, agricultural soils in many parts of the world are exposed to low or moderate cadmium accumulation. Due to its high mobility in water and the soil–plant system, cadmium can easily be included in the food chain; thus, it can be dangerous for plant, animal and human health. The sources of cadmium in the air are the burning of fossil fuels such as coal or oil and waste. Cadmium can also be emitted into the air as a byproduct of the smelting of ores such as zinc, lead or copper. Cadmium in the atmosphere is also increased by the burning of nickel-cadmium batteries and the use of cadmium dyes.

Various salts of cadmium (acetate, bromide, fluoride, iodide, carbonate, chloride, nitrate, oxide, salicylate, cyanide, tungstate) are free or in the form of alloys with zinc, nickel, silver and lead. They are used in cells, accumulators, porcelain, nuclear material, amalgam in dentistry, plastic, metal coating, vacuum tubes, photographic materials etc. Cadmium oxide and anthranilate are used as anthelmintic agents in pigs and chickens in production and veterinary medicine [1, 30–32].

Poisoning with cadmium occurs by inhalation of dust or vapors at low concentrations over a long period of time and ingestion of dissolved cadmium and its salts mixed with food. Smoking is an important source of cadmium exposure. Smokers have twice as much cadmium in their bodies than non-smokers. For non-smokers, food is the largest source of cadmium exposure. Cadmium levels in some foods can be increased by applying phosphate fertilizer or sewage sludge to agricultural areas. The dark brown fumes that occur when cadmium is heated outdoors cause poisoning. The presence of cadmium's main mineral compounds in the environment or workplace air causes occupational diseases [1]. In the most obvious example of Cd poisoning today; in the city of Toyama, Japan, 200 people were shown to have permanent bone and kidney disorders due to severe Cd poisoning due to excessive consumption of Cd-contaminated rice [33].

Cadmium poisoning is on the occupational diseases list in EU countries. The Japanese named cadmium poisoning itai itai (pain-pain) disease. The EPA considers cadmium to be a possible human carcinogen (cancer-causing agent) and classified it as a Group B1 carcinogen [34].

2.5 Chromium and chromium compounds

Chromium (Cr) is a gray solid steel with a high melting point and atomic weight of 51.996 g/mol. It has oxidation steps ranging from chromium (-II) to chromium (+VI). It forms a large number of compounds in both chromium (III) and chromium (VI) forms. Chromium compounds are stable in the trivalent state and the hexavalent form is the second most stable state. While chromium (VI) compounds are easily soluble in water, chromium (III) compounds are slightly soluble in water and the water-soluble part can be found as chromium (III) complexes. Chromium is an element naturally found in rocks, animals, plants, soil, volcanic dust and gases. It is mostly in the form of naturally occurring chromium (III), which is an important nutrient, and chromium (VI), most commonly produced by industrial processes, along with the lesser known metallic chromium (0). Chromium (III) is essential for normal glucose, protein and fat metabolism and is therefore an essential dietary element. Chromium (III) is an essential element that should be consumed daily by adults at 50–200 μg/day. The body has various systems to reduce chromium (VI) to chromium (III). The most important industrial chromium sources in the atmosphere are related to ferrochrome production. Metal chrome is mostly used to make steel and other alloys. Chromium compounds in chromium (III) or chromium (VI) forms are used for chrome plating, paint and pigment production, leather and wood protection, and treatment of cooling tower water. It is used for toner for copiers and in smaller quantities in various industries such as drilling muds and textiles. The general population is exposed to chromium (chromium (III) in general) by food and drinking water and breathing air containing chemicals. Chromium (VI) is much more toxic than chromium (III) for both acute and chronic exposure. The respiratory tract is the primary target organ for chromium (VI) following inhalation exposure in humans [1, 35, 36]. The EPA concluded that only chromium (VI) should be classified as a human carcinogen. Animal studies show that chromium (VI) causes lung tumors with respiratory exposure. The EPA classified chromium (VI) as Group A, a known human carcinogen, for inhalational exposure. There is no data on the carcinogenic potential of chromium (III) compounds. The EPA classified chromium (III) as group D [37].

2.6 Nickel and nickel compounds

The chemical symbol for nickel is Ni and its atomic weight is 58.71 g/mol. It is a silvery-white hard metal found in nature as a component of silicate, sulfide or arsenide ores. Nickel is found in the environment primarily with oxygen or sulfur as oxides or sulfides. The most common form in nature is the Ni + 2 state. Each form of nickel has different physical properties. Soluble nickel salts include nickel chloride, nickel sulfate and nickel nitrate. Nickel carbonyl, an extremely unstable form, does not occur naturally and decomposes rapidly. Since nickel is a natural element in the earth's crust, it is found in small amounts in food, water, soil and air. Foods are the main sources of nickel exposure. Average intake for adults is approximately 100–300 μg/day. In addition, people working in professions involved in the production, processing and use of it, or people who come into contact with everyday products such as jewelry and stainless-steel cooking and dining utensils containing nickel, and who consume cigarette tobacco may be exposed to nickel. The most toxic nickel compound is nickel carbonyl (Ni (CO)4). Nickel carbonyl, used in the metallurgy and refining industry, is obtained by the reaction of metallic nickel with CO2. If air inhaled for 20 minutes contains 30 ppm of nickel carbonyl, it can lead to lethal toxic effects [1, 38, 39]. Nickel is found at very low levels in ambient air as a result of emissions from oil and coal burning, nickel refining, sewage sludge burning, production facilities and other sources. Due to its high instability, nickel carbonyl exposure is extremely rare. In industry, it is used in electroplating, batteries, (cadmium-nickel mixture) coins, industrial installations, spark plugs, machine parts, stainless steel, nickel-chromium resistance wires and catalysts [1, 40].

Nickel salts, nickel sulfate via inhalation and drinking water and nickel acetate are not carcinogenic in rats or mice. The EPA has not evaluated soluble salts of nickel for potential human carcinogenicity. Lung tumors were reported to develop in rats exposed to nickel carbonyl through inhalation. The EPA classified nickel carbonyl as group B2, possible human carcinogen. An increased risk of lung and nasal cancer was reported for nickel refinery powders and nickel subsulfide among nickel refinery workers. Nickel refinery powder is a mixture of many nickel compounds, the main component being nickel subsulfide. Additionally, animal studies reported lung tumors due to nickel refinery dust and nickel subsulfide exposure. The EPA classified nickel refinery powder and nickel subsulfide as group A human carcinogens [41].

3. Mitigation of heavy metals

Heavy metal toxicity caused by various anthropogenic and geological activities poses a global threat to the environment and people [42]. Humans have long used chemical, physical and biological methods to combat the threat of heavy metal toxicity, both to humans and the surrounding environment [8]. For example, in the literature, Spirulina (Arthrospira), a photosynthetic thread-like cyanobacterium commonly known as blue green algae, was shown to attenuate experimentally-induced heavy metal toxicity. A total of 58 preclinical studies demonstrated the mitigating effect of Spirulina against experimental arsenic, cadmium, lead and mercury toxicities [42]. Some important antioxidants such as flavonoids, pectin, and phytic acid are also used to remove heavy metals from the human body [43].

The removal of heavy metals from environmental compartments has become an extremely important issue. Current cleaning (or remediation) technologies to reduce harmful effects in heavy metal-contaminated areas include excavation (physical removal of the contaminated material), stabilization of metals in the site soil, and the use of plants to stop the spread of contamination or remove metals from the soil (bioremediation). Along with a range of phytochemicals, microorganisms are thought to be able to act as heavy metal removal agents in both humans and the surrounding environment [43]. The bioremediation approach is an effective method for removing toxic wastes from the environment using biological agents. It can help remove many contaminants such as metals, pesticides, explosives and oil compounds. It is mostly performed on-site and is widely accepted. Microorganisms and plants use different mechanisms for bioremediation of contaminated water and soils [44–46]. The bioremediation process occurs through a variety of mechanisms like redox, adsorption, complexation, ion exchange, precipitation and electrostatic attraction [47]. Microorganisms may begin metal mobilization/immobilization with redox reactions and hence affect bioremediation processes. Heavy metals like Fe, As, Cr and Hg enter oxidation and reduction cycles. Remediation of heavy metals from water uses microorganisms including algae and bacteria, along with fungi (*Aspergillus sp., Saccharomyces cerevisiae* etc.) and consortium organisms (Acinetobacter sp. & Arthrobacter sp., P.aeruginosa & B.subtilis, S.cerevisiae & P.aeruginosa, S.cerevisiae and B.subtilis). Biosorption by bacteria ((*Bacillus*), cocci (*Streptococcus*), filamentous (*Actinomyces*) and spiral (*Vibrio cholera*)) is an inexpensive and efficient technique to remove pollutants, like heavy metals, from wastewater [48, 49]. Different species of algae are present in large amounts in marine ecosystems [50]. Among the three algal groups, i.e., Phaeophyta, Rhodophyta and Chlorophyta (i.e. brown, green and red, respectively), brown algae were reported to possess better biosorption capacity (phycoremediation) [51, 52].

Phytoremediation is proven to be a promising alternative to traditional approaches as it is cost effective, environmentally friendly and esthetically pleasing. To date, approximately 500 taxa were identified as hyperaccumulators of one or more metals based on their natural extraction ability. In addition, more research is needed that integrates biotechnological approaches with extensive multidisciplinary research to improve plant tolerance and reduce toxic metal deposition in the soil [8, 53]. In the agricultural field, phytoremediation, phyto-extraction, phyto-polymerization, phytostabilization, phytodegradation and rhizophilization are effectively used for the removal of heavy metals [45]. Plants also help prevent wind, rain, and groundwater runoff from carrying pollutants from the site to the surrounding areas or deeper underground [46] (**Figure 1**). Silicon (Si) is the second most abundant element in the soil. Research to date suggests that Si can alleviate heavy metal toxicity in plants at both plant and soil levels, with the use of Si supplementation providing a beneficial role in reducing abiotic factors, including heavy metal stress, as well as stress exerted by biota [54, 55].

Integrated processes are a combination of two different methods to achieve a synergistic and effective method to remove heavy metals. Combining both microorganisms and plants is a bioremediation approach that enables more efficient

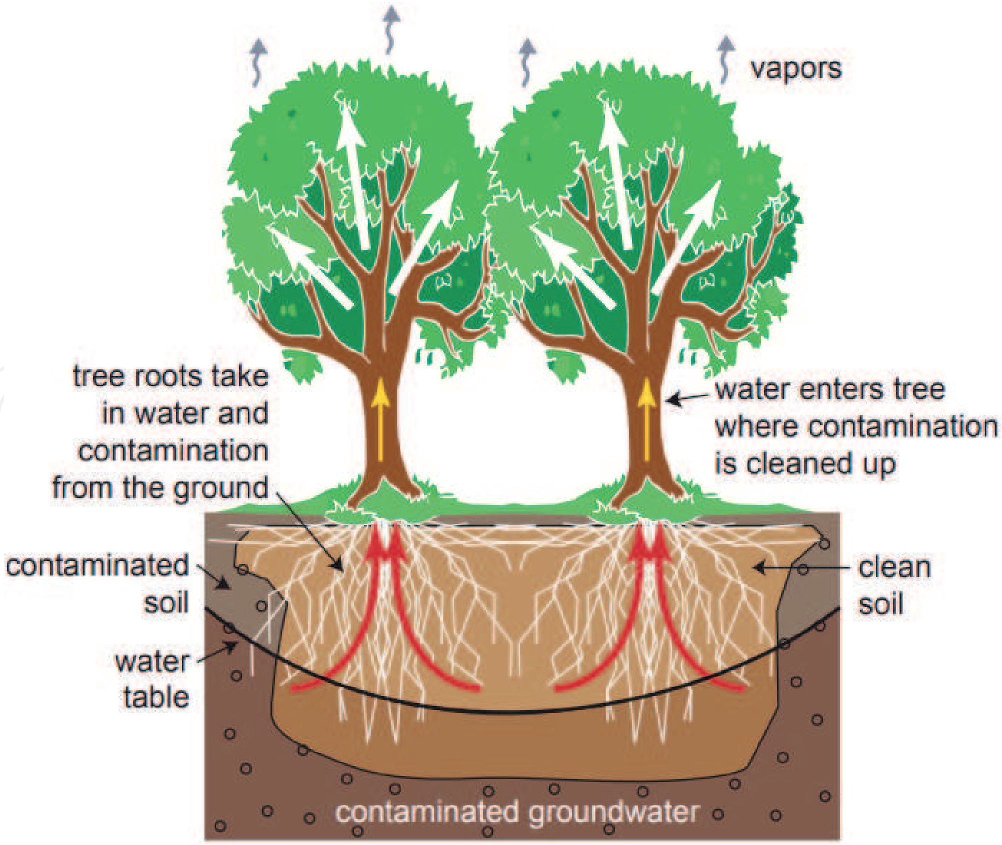

Figure 1.
Mitigation of heavy metal pollution [46].

cleaning of heavy metal contaminated soils. However, the success of this approach largely depends on the organisms involved [44, 56].

4. Conclusion

Heavy metal pollution in water and soil has increased in the last few decades due to anthropogenic activities. For this reason, the issue of dealing with heavy metal pollution in environmental matrices still maintains its importance. Legal regulations are enforced by governments, and monitoring studies, assessment of environmental impacts, use of soluble and non-toxic compounds in environmental compartments (air, water, soil and plants) in industrial processes, heavy metal-free pesticides, appropriate wastewater treatment plants and renewable energy sources instead of fossil fuels are priority measures to reduce the concentrations of heavy metals in the environment. In addition, heavy metals, which cause serious health problems even at very low concentrations due to their long-term persistence, must be removed from receiving environments in order to protect the integrity of the ecosystem and human health. As a bioremediation approach, removing toxic wastes from the environment by using bioaccumulatory organisms such as plants or mussels maintains its importance among studies aimed at recovery. Studies have shown that integrated methods - especially the combination of suitable plants and microorganisms - are very effective in mitigating the effects of heavy metals in the environment.

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