

### **IMPACT OF HEAVY METAL POLLUTION ON THE BIOTIC AND ABIOTIC COMPONENTS OF THE SOIL ENVIRONMENT**

#### **ABSTRACT**

The environment comprises biotic and abiotic components interacting as a system. The environment contains organic and inorganic minerals in the optimal concentration required by living organisms for growth, development, and metabolic activities. Due to anthropogenic activities and some natural occurrences, the availability of these elements has drastically increased in the ecosystem beyond the threshold and permissible limits causing pollution. Heavy metal (HM) is one of the naturally occurring elements that threaten plant, animal, and human health. These HMs have been defined as elements with more than  $5\text{gcm}^{-3}$  relative density that are not readily biodegradable but can be transformed from one state to another and are usually associated with toxicity or ecotoxicity. However, some heavy metals are biologically essential elements required in the body/plant or as constituents of important enzymes although in trace amounts while others are non-essential and are ranked as priority metals due to their high level of toxicity with no biological importance even at low concentrations. The non-degradability property of heavy metals contributes to its persistence and subsequent accumulation in the biota and the food chain which is of public health significance to humans and animals. The soil environment is highly prone to HM contamination due to physiological, biochemical, metabolic, and biogeochemical processes that occur within the environment mostly mediated by microbes. These microbes are inarguably the drivers of ecosystem functioning, although are significantly the most affected by HM pollution. This review, therefore, describes the ecotoxicological effect of heavy metals with special reference to the soil environment. Other sections discussed are the toxicity and general properties of some selected heavy metals as environmental pollutants and essential elements. In addition, the effect of HM on soil microbes was analyzed in two folds: i) reduction in microbial population and diversity and ii) increased diversity and abundance of HM-resistant microbial strains which are significant in bioremediation.

Keywords: Heavy metal, pollution, environment, microorganisms, ecotoxicology

#### **Introduction**

Heavy metals are metallic elements known to have a density higher than that of water [1]. They are present naturally in water and land in very small concentrations with a ppb of  $< 10\text{ppm}$  and are therefore referred to as trace elements [2]. Although heavy metals can occur

naturally in the environment, they can also be introduced or increased in the environment as a result of anthropogenic activities such as mining, smelting operations, agricultural activities, and the use of other metal-containing compounds [3]. Other natural sources of HM pollution of the environment include volcanic eruptions, weathering of metal-bearing rocks, and metal corrosion. In addition, some of the severe environmental consequences of heavy metal contamination occur through metal ion soil depletion, sediment re-suspension, and heavy metal leaching. However, weathering and volcanic activities have been shown to contribute considerably to heavy metal contamination [3]. Other industrial sources of heavy metal pollution include the combustion of coals and petroleum in power plants, quarries, metal processing in refineries, nuclear power plants, high-tension lines, plastics, textile, and paper processing industries [4].

Heavy metals can be categorized into essential and non-essential metals based on their uses and requirements by biological entities. The essential heavy metals act as macronutrients such as zinc (Zn), copper (Cu), nickel (Ni), cobalt (Co), and chromium (Cr) and they also play a key role in oxidation-reduction reactions [5] while non-essential heavy metals include cadmium (Cd), lead (Pb), plutonium (Pu) and mercury (Hg). These metals have no biological importance and are thus regarded as environmental pollutants [6]. Although, plants, humans, and microorganisms utilize heavy metals for metabolic and physiological functions, at high concentrations they are toxic and could be damaging to organs. For example, copper (Cu) is an essential cofactor to numerous enzymes responsible for reactive oxygen species (ROS) homeostasis due to its ability to inter-convert or reduce Copper II to I oxidation state. Nevertheless, this same attribute of ROS production by copper could lead to oxidative stress when it is present in high concentrations. According to United States Environmental Protection Agency (USEPA 2020), the limit for HMs in soil and for oral doses are 1600 mg kg<sup>-1</sup> and 20 µg Kg<sup>-1</sup> day<sup>-1</sup> for Ni, 78 and 1 for Cd, 0.31 and 3 for Cr, 400 and N/A for Pb, 0.77 mg kg<sup>-1</sup> and 0.33 µg Kg<sup>-1</sup> day<sup>-1</sup> for As and 11 and N/A for mercury [7].

Different metals have unique physicochemical characteristics which contribute to their toxicological modes of action, toxicity, and carcinogenicity to biotic environmental components through diverse mechanisms although still yet to be fully understood [8]. Some of these physical characteristics which affect heavy metal bioavailability and toxicity include temperature, phase association, adsorption and pH while the chemical parameters include, speciation of thermodynamic equilibrium, water partition coefficients, lipid solubility and complexation kinetics. The biological aspects such as physiological/biochemical adaptability and special traits also have major impacts on the toxicity of metals in any environment [9]. The type of soil in which the heavy metal pollution occurs is also a major factor in the toxicity of the metals. This is because different soil types have different propensities to accumulate, release and make heavy metals available [10].

The disruption and acceleration of natural geochemical sport processes caused by phylogenic activities such as mining has resulted in heavy metal accumulation far above recommended concentrations in the environment [11]. Heavy metals released by geothermal activity, agricultural and domestic wastewater, as well as varying amounts of unmanaged flows from industrial waste disposal systems, may seep into the groundwater [12, 13]. Continuous seepage of these metals into groundwater over time can cause increased accumulation of the metals and thus escalating the concentrations to a level far beyond the acceptable recommendations [14].

Various biological and toxicological effects of heavy metals in the environment occur as a result of the diverse forms in which heavy metals interact and exist in the environment. The consequence of elevated levels of HM contamination sometimes leads to the overall reduction in microbial activity, population, and diversity in the environment [15]. Again, increased HM toxicity can result in the modification of the structure of proteins or nucleic acids in living organisms. Mercury, cadmium, and silver can hinder the activity of certain enzymes that are necessary for microbial metabolism by attaching to the sulfhydryl (SH) groups [16]. The impacts of the heavy metals can range from the inhibition of microbial metabolism, morphology, growth, and destruction of the integrity of bacterial plasma membrane [16]. Other impacts of elevated heavy metal concentrations in soil and water may include a reduction of soil protein activity, soil microbial activity, and thus a reduction in the soil microbial community. Soil microbes are essential in soils because they support ecosystem functioning and mediate several metabolic and physiological processes in the environment. Some of these roles include decomposition of soil organic matter, regulation of biogeochemical cycles, biotransformation and bioconversion of elements, nutrient uptake, bioremediation, and others. Hence, any slight decline in the abundance or diversity of these microbes could have a profound impact on the ecosystem and its components [17]. To understand the dynamics of soil microbial communities, it is important to first identify their structure, abundance, and distribution. Additionally, in-depth knowledge of the microbial arrangement and their response to changes in environmental conditions due to heavy metal contamination is also important to understand the soil microbial community and response [18].

In the contemporary world, the safety and protection of the environment are of foremost importance. For this reason, scientists are making improved efforts to develop technologies that can help to improve and enhance the management of HM contamination in the environment. Studies on the impact of HM on soil, plants, and water have been reported by several researchers [19, 20]. In plants, HM acts as macro and micronutrients which play essential roles in the biochemical and physiological processes of plants which include:

nitrogen fixation, DNA synthesis chlorophyll biosynthesis, protein modifications, and redox reactions in the chloroplast and the mitochondrion, photosynthesis, and sugar metabolism. Zinc for example is a cofactor for more than 300 enzymes and 200 transcription factors responsible for reproduction, auxin metabolism, and maintenance of membrane integrity [21, 22] However, at elevated concentrations, the essential heavy metals produce severe toxicity symptoms in plants [22, 23] while the non-essential category is toxic to plants even at low concentrations. In soil, when HM pollution occurs, it is transported around the soil and its fate is dependent significantly on the speciation and chemical nature of the metal. The initial step involves a very swift reaction (minutes, hours) immediately followed by a slow adsorption reaction occurring for days or months. The HM is subsequently redistributed into various chemical forms with different toxicity levels, bioavailability, and mobility. It is believed that the several reactions of the heavy metals in soil control distribution such as plant uptake, mineral precipitation and dissolution, biological immobilization and mobilization, ion exchange, and aqueous complexation [24].

In addition to adverse impacts on plants and soil, heavy metals pose threat to human health due to their persistence in nature. For instance, Pb is one of the most toxic heavy metals that have a soil retention time of 150–5000 years and have been reported to maintain its high concentration for as long as 150 years [25, 26]. Plants growing in heavy metal-contaminated sites generally accumulate a high quantity of heavy metals, and thus, contamination of the food chain occurs which can result in the entry of heavy metals into animal and human tissues, making them prone to several diseases that range from dermatitis to various types of cancers. This problem might become even worse if sufficient measures are not taken at the right time.

Research in heavy metal contamination in the environment is driven by the hope to decrease the entry of heavy metals into crop plants, and water bodies thereby reducing the risk of contamination in animals and human beings. The majority of the studies conducted have used both culture-dependent and independent methods to determine the effects of heavy metal contamination on the soil microbial community. The results of these experiments have been inconsistent which could be relatable to the different biological, physical, and chemical conditions influencing the process. Some researchers have reported an increase in microbial diversity while in other reports, reduction in diversity, richness, and abundance, as well as diversity shift, has been documented [27, 28, 29]. Alirzayeva *et al.* [30] recommended that since heavy metal toxicity can directly or indirectly limit the growth and development of plants as a result of a reduction in the rhizospheric microbial population, the interactions between plants and heavy metal tolerant microorganisms such as antibiosis and the induction of systematic resistance can be harnessed to reduce metal toxicity. Plant-

associated microbes such as rhizospheric microbes (plant growth promoting rhizobacteria, PGPR), endophytic microbes, and arbuscular mycorrhizal fungi have the ability to alter the bioavailability of heavy metals through the production of chelating agents, the release of acids, phosphate solubilization and changes in redox potential [20]. This review, therefore, captures heavy metals as an environmental pollutant and their ecotoxicological effect on the different biotic and abiotic components of the environment. Also, the properties and toxicity of different selected essential and non-essential heavy metals have been highlighted and eco-friendly heavy metal bioremediation strategies discussed.

### **Heavy metal pollution**

Environmental pollution caused by heavy metals is considered to be one of the foremost challenges in modern human society [31]. Technological advancement, urbanization, and industrialization have led to a drastic increase in heavy metal contamination. Some of the natural sources by which heavy metals are introduced into the environment include volcanic eruptions and the weathering of metal-containing rocks while anthropogenic sources include mining, smelting, release from industrial effluents, domestic activities, and other agricultural activities which include the use of metal-containing fertilizers and pesticides [10, 11]. According to Cullen *et al.* [32], the combustion of fossil fuels could also lead to an increase in the release of cadmium (Cd) into the environment.

Due to their toxicity, heavy metals remain in the environment, pollute food chains, and create a variety of health concerns. Long-lasting exposure to heavy metals in very high concentrations in the environment can pose a serious threat to humans, plants, animals, and microbes. Copper, arsenic, zinc, silver, chromium, molybdenum, mercury, gold, vanadium, cadmium, and lead are examples of heavy metals [33, 34]. The properties of some selected heavy metals will be discussed as follows:

#### **Lead (Pb)**

Lead is one of the oldest metals to be used by humans, dating back to 6500BC. In a report by El-gohary [35], lead pipes were used to make glazes in potteries in Egypt during the time of pharaohs and also for the construction of water pipes. Lead is a naturally occurring element that makes up about 0.0013% of the earth's crust. It is frequently found in combination with other minerals, particularly zinc, silver, and copper. Other elements, such as gold, can also be found in trace amounts in lead ore [36]. Galena, or lead sulfide, is the most common lead ore which is mostly mined, concentrated, and then smelted using limestone and coke in a blast furnace. It is further refined to get rid of impurities and to recover additional metals [36]. Secondary or recycled lead is currently and has been for years, a key role in the lead market due to its ease of re-melting and refinement. In the United States, roughly 80% of all

lead is used in automotive-type batteries, and these batteries are mostly not disposed off properly and can therefore cause heavy metal pollution in the environment [37].

Lead is a common contaminant found in soil and unlike other metals, it is toxic to biotic elements has no biological role in the environment. Uptake of lead in food, water, and air are the most significant ways by which lead enters the human body and the constant exposure to these metals can lead to severe effects on the health of plants and humans [38]. Exposure of humans to a very high level of lead may produce encephalopathy [39]. In most cases, repetitive or continued exposure to lead can cause toxic stress on the kidney, which if untreated may result in irreversible and chronic intestinal nephritis [39]. Lead exposure has also been reported as a major factor that may contribute to the development of hypertension. Wildemann *et al.*, [40] also discovered that increased lead exposure can heighten the risk of hypertensive heart disease and cerebrovascular diseases.

The effects of lead contamination on plants have been reported by several researchers. According to Sengar *et al.* [41], lead could be solubilized and transported into leaf cells causing inhibition in the intracellular physiological processes of the plant. Numerous kinds of research have been conducted using lead amended soils and hydroponic cultures, majority of these systems have shown a significant reduction in the growth and development of several plants following an increase in the lead concentration of the soil or hydroponic system. *Avena sativa*, a very sensitive rice specie, showed a 34 percent decrease in fresh weight, a 23 percent decrease in dry weight, and a 26 percent decrease in chlorophyll content [42]. The plant length was also reduced by 34 percent and the root length was reduced by 70 percent when grown in nutrient solution emended with  $10^{-4}$ M in lead nitrate  $Pb(NO_3)_2$  with  $10^{-4}$ M lead chloride ( $PbCl_2$ ) treatment for 21 days [42].

### **Nickel (Ni)**

Nickel is the 23rd most abundant element in the Earth's crust, and it is the 5th most abundant element regarding weight after iron, oxygen, magnesium, and silicon and the 28th element in the periodic table (95). It is found primarily as oxides or sulphides in the environment [43]. Nickel is a hard, silvery white metal with qualities that make it ideal for combining with other metals to form alloys. Nickel and its derivatives do not have a distinct odor or flavor. It can be alloyed with chromium, copper, zinc, and iron, among others, and these alloys are used in a variety of applications, including the production of metal coins and jewelry. Nickel is also utilized in the manufacturing of valves, heat exchangers, and stainless steel. Nickel, in combination with other elements, can be found naturally in the earth's crust, in all soils, and can also be emitted by volcanoes. It can also be found in meteorites and seafloor nodules, which are mineral lumps on the ocean floor [43]. Mining and enterprises

that transform scrap or fresh nickel into alloy discharge nickel into the atmosphere, and this is one of the major ways by which nickel is released into the environment. Nickel is also discharged into the atmosphere by oil and coal-fired power plants, as well as garbage incinerators [44].

In concentrations above recommended levels, exposure to nickel can cause several damages to the environment, plants, humans, and microorganisms. Nickel damage to humans has long been associated with oxidative reactions involving lipids, proteins, and DNA, it has also been found to attach to biomolecules and thus alter their properties [45]. Some of the mechanisms by which nickel affects microbial cells include: replacing essential metals, binding to non-metal enzyme residue, binding outside the catalytic sites of an enzyme, and causing oxidative stress in lipids, DNA, and proteins [45]. However, according to Nieminen *et al.* [46], the mechanisms of nickel toxicity in microorganisms have been understudied, despite the widely demonstrated toxic effect of this metal and thus further research on the toxicity of nickel is recommended.

### **Zinc (Zn)**

Zinc (Zn) is a mildly brittle metal at ambient temperature and has a bluish-white, glossy, diamagnetic property [47]. It is a good electrical conductor and has low melting (419.5 °C) and boiling temperatures (907 °C). Zinc is the 24th most abundant element, accounting for 75 parts per million (0.0075 percent) of the Earth's crust. Zinc levels in soil range from 5 to 770 parts per million, with an average of 64 parts per million. Its levels in seawater are about 30 ppb, while the atmosphere holds 0.1–4 g/m<sup>3</sup> of zinc [41]. In ores, the element (zinc) is usually found in combination with other base metals like copper and lead.

Zinc is the fourth most produced metal and is essential to modern living. Its uses range from its application in rubber production and pharmaceuticals, metal coatings to protect iron and steel from corrosion, and also as an important element for enhanced growth in animals, plants, and humans [48, 49]. Although zinc is important for human health and development, it can also be harmful if found in excess in the environment. Zinc ions in solution can be toxic to plants, animals, and other invertebrates [50]. During anthropogenic activities such as mining, chemical, pulp, and paper production, Zn<sup>2+</sup> is usually emitted and can be extremely harmful to the environment and creatures exposed to it [51]. Zinc concentrations in the soil exceeding 500 parts per million (ppm) impede plant absorption of other critical elements like iron and manganese [46, 52]. Inhaling zinc fumes while brazing or welding galvanized objects can cause a condition known as the zinc shakes or "zinc chills." Zinc is a frequent ingredient in denture cream, and it can range from 17 to 38 milligrams per gram. Excessive usage of these products has been linked to disability and even death. According to reports by The U.S. Food and Drug Administration (FDA), zinc damages nerve receptors in

the nose, causing anosmia as observed in the 1930s when zinc preparations were used in a failed attempt to prevent polio infections [53].

## **Copper**

Copper is one of the most utilized metals in the world and on the list, it is third. Copper is one of the essential heavy metals and it is categorized as a micronutrient. Its application cuts across humans, animals, and plants. It is required in the growth of plants and animals and in humans, it assists in the formation of blood hemoglobin. Again, in plants, Cu is specifically important in areas that support plant growth such as disease resistance, seed production, and water regulation. Notwithstanding, Cu even as an essential metal can cause a number of health issues such as kidney damage, stomach, and intestinal irritation, anaemia, regulation of water, liver and kidney damage when present in elevated concentrations [38]. It has been reported that there is a complex but defined interaction between copper and the environment [54]. When Cu is introduced into an environment, it immediately becomes stable and takes up a form that is not toxic, harmful, or poses any risk to the environment, unlike some other metals. In addition, Cu does not bioaccumulate in the food chain which is one of the public health challenges in heavy metal pollution and also it is not magnified in the body. This essential heavy metal forms strong complexes with soil which indicates only a small fraction is present in soil solution and they occur as Cu (II) [54].

Another important aspect of Cu is in the treatment of water. In recent times Cu has been used in the treatment of drinking water and transportation due to its known antimicrobial activity. In 2008, it was recognized by the American Environmental Protection Agency as the first metallic antimicrobial agent and since then, research on copper as an antimicrobial agent has gained attention. A number of studies have shown very impressive results using copper surface and copper particles as treatment options. Copper when in excess in water can be removed up to 97-98% with a reverse osmosis water filter or activated carbon using adsorption method [55].

### **3.7. Mercury**

Mercury (Hg) is a non-essential HM and it is found on the periodic table with Zinc and Cadmium. Mercury is characterized by atomic weight of 200.6, atomic number of 80, melting point of  $-13.6^{\circ}\text{C}$ , and boiling point of  $357^{\circ}\text{C}$ , density of  $13.6\text{ g cm}^{-3}$ , and is usually recovered as a byproduct of ore processing. There are several sources of Hg in the environment but the major source of Hg contamination is the release from coal combustion. Another contributor to Hg contamination is the release from manometers at pressure-

measuring stations along gas/oil pipelines. In the environment, Hg exists in different forms such as mercurous ( $\text{Hg}_2^{2+}$ ), mercuric ( $\text{Hg}^{2+}$ ), alkylated (methyl/ethyl mercury), or elemental form ( $\text{Hg}^0$ ) [24]. These various forms are initiated based on the pH and redox potential of the system. Organic and inorganic mercury could be reduced to elemental Hg and further converted to other alkylated forms by abiotic and biotic processes.

The redox potential and pH of the system determine the stable forms of Hg that will be present. Mercurous and mercuric mercury are more stable under oxidizing conditions than under mild reducing conditions. Mercury properties and toxicity vary in the different forms in which they occur. In the alkylated form, Hg is most toxic, soluble in water, and volatile in air. Mercury (II) is very soluble in oxygen-rich aquatic environments and this is because of the strong complexes formed with different organic and inorganic ligands. This phenomenon can increase the toxicity level of Hg in water. Mercury may be removed from the solution through different mechanisms such as sorption to humic materials, soils and sediment, and this process is pH dependent. Another mechanism of Hg removal from solution is through co-precipitation with sulphides. Microorganisms such as sulfur-reducing bacteria also play key roles in the conversion of organic and inorganic forms of Hg to alkylated forms under anaerobic conditions. Under similar conditions of no oxygen, elemental Hg may be produced by reduction of mercury (II) or by demethylation of methyl mercury. Elemental mercury is liquid at room temperature and can be readily evaporated to produce vapor. Mercury vapor is more hazardous than liquid form. Methyl Hg can also be formed under acidic conditions ( $\text{pH} < 4$ ) and higher pH encourages the precipitation of Mercury sulphide ( $\text{HgS}$ ). Severe medical conditions have been associated with mercury such as bloody diarrhea, kidney failure, and abdominal colic pain [56].

Mercury compounds have several applications such as in the production of fluorescent light bulbs in lamp manufacturing companies, and in mining industries for the extraction of gold and other industrial resources. Methyl- and ethyl-mercury have also been reportedly used as fungicides to combat phytopathogens. In the past, mercury served several medicinal uses, although such medications are no longer in use and have been replaced by safer medicines. Such drugs include mercurophylline, phenylmercury nitrate (disinfectant), chlormerodrin, and merbaphen. Also, mercury has also been used in the production of some cosmetic products such as lightening creams and soap. Mercury chloride is the major active agent in the formulation of skin brightening cream [40].

### **The fate of heavy metals in the ecosystem**

A few heavy metals have been designated as essential metals because they are beneficial to the growth of organisms and can also play major roles in a number of physiological and biochemical processes [57]. These heavy metals have been widely employed in industries, agriculture, medicine, and other fields resulting in their dispersion into the environment, including the air, water, and soils. Anthropogenic activities have also resulted in extremely high metal concentrations in contaminated locations such as abandoned mines which drastically increases the toxicity level in such environments. Heavy metal toxicity rises as a result of the concentration of a large amount of the metal in one place and hence can lead to limited vegetation of the location and a reduction in the diversity of the organisms in such environment to only heavy metal tolerant species [58].

Metals cannot be broken down since they are non-biodegradable and hence exist in the environment for a long period. Heavy metals in soils and sediments stay in the environment for a long time before being eluted to other compartments. They can be transformed in the presence of other elements in the soil or sediment, making them more poisonous such as in the synthesis of methyl mercury from inorganic mercury. Humans are exposed to heavy metals during manufacturing, industrial, and pharmaceutical processes, on farms, and even in residential areas. These heavy metals can get into the human systems via direct skin contact with contaminated farm tools, inhalation of contaminated air, ingestion of polluted food, etc. [59]. Heavy metals can bioaccumulate in organisms' systems after being swallowed or inhaled and can result in biological and physiological difficulties [60]. A few essential metals are required for the creation of skeletal structures, the regulation of acid-base equilibrium, and the preservation of the colloidal system [61]. They are also crucial as components of important enzymes, structural proteins, and hormones. For example, zinc is a component of numerous enzymes, iron, which is required for hemoglobin, and selenium, and is an essential requirement for the glutathione peroxidase enzyme [62]. Although non-essential metals have no role in the body, they can induce toxicity by affecting the level of an essential element in the body [63].

### **Arsenic**

Arsenic has a low crustal abundance (0.0001%) in nature and is frequently associated with metal ores such as copper, lead, and gold [64]. Arsenic is a common element that is found in abundance in the earth's crust, seawater, and the human body [65]. Arsenate, As (V), Native elemental arsenic As (0), Arsenite As (III), and As(-III) are the four oxidation states of arsenic [64]. Although elemental arsenic is rare, toxic arsines can be found in gases emitted by anoxic environments. In aqueous, aerobic environments, arsenate is the most common form of inorganic arsenic. Certain pollutants, such as arsenic (As), can persist in the

environment for a long time. They eventually build up to levels that can harm the physiochemical properties of soils, resulting in a loss of soil fertility and crop yield. When arsenic is not detoxified, it can cause a chain reaction that inhibits growth, disrupts the photosynthetic and respiratory systems, and stimulates secondary metabolism [66].

Arsenic contamination of water and soil can also have a negative impact on food safety. Accumulated arsenic in plants affect the growing mechanisms and hence the yield of crops, as well as the accumulation of arsenic in crops may impact on health of living beings. Also, the accumulation of As in soil caused by the use of As-contaminated irrigation water has been shown to result in elevated levels of As in paddy soil and soil solution [67]. Panauallah *et al.* [68] conducted a study to determine the impact of As contaminated irrigation water on soil As content and rice productivity over two winter-season rice crops in Bangladesh. Results indicated a decline in yield progressive from 7–9 to 2–3 t ha<sup>-1</sup> with increasing soil-As concentration.

## **Cadmium**

Cadmium (Cd) is a post-transition element in group IIB of the periodic table and is commonly found in zinc ores [69]. It ranks seventh among the top 20 toxic metals and is classified as a group 1 carcinogen. It is one of the most dangerous metals due to its high toxicity and extensive bioaccumulation [70, 71]. Cadmium is a relatively volatile white lustrous and tarnishable element with melting and boiling points of 321 and 767°C, respectively, and a heat of vaporization of 26.8 Kcal mol<sup>-1</sup>. Cadmium is not an essential nutrient and inhibits plant growth at high concentrations. It has also been reported that it alters plant metabolism even at low concentrations [72].

It has been reported that high Cd concentrations reduces cell growth as well as overall plant growth. In a study by Al-Yemens *et al.* [73], *Vigna ambacensis* was treated with a low concentration of Cd, and the root and shoot mass decreased significantly. High Cd content in soil can affect soil fertility, plant physiology, and metabolism, resulting in plant growth retardation and decreased yield [74]. Cd also disrupts ion homeostasis by inhibiting the absorption of basic ions such as iron and magnesium, influencing nitrogen metabolism, and reducing water and mineral uptake [75]. It also has a negative impact on photosynthesis, mineral element uptake, and transportation, resulting in a decrease in yield [76]. It can cause morphological, physicochemical, and structural changes in plants, such as inhibiting lateral root formation, chlorosis, and stomatal density [77]. Cadmium interferes with mitochondrial

function by impairing redox regulation, which damages membrane lipids and disrupts plant metabolism

### **Effect of heavy metal contamination on the environment**

Heavy metals contaminate freshwater bodies, sediments, and soils once they are released from both natural and human activities, hence both terrestrial and aquatic ecosystems are threatened by toxic metals [78]. Heavy metals discharged into the atmosphere as a result of volcanic eruptions and various industrial emissions eventually fall to the ground, contaminating water and soils. These metals accumulate in biota or leach into groundwater and their presence and persistence in these environments have serious consequences for public health [79]. Different physicochemical and climatic factors affect the overall dynamics and biogeochemical cycling of heavy metals in the environment and it is therefore critical to determine the extent of heavy metal contamination in the ecosystem by examining the concentrations and distribution of these elements on the different biotic and abiotic environmental compartments [80].

### **Effect of Heavy metal on water**

Water is a universal solvent and hence it can dissolve diverse environmental contaminants including inorganic and organic chemicals. Aquatic ecosystems such as the marine and freshwater systems are easily contaminated and termed "the ultimate sink for contaminants". Contamination of the water environment results majorly from anthropogenic activities such as agriculture (pesticides, fertilizers), urbanization (deforestation, automotive activities), and industrialization (mining, construction, refining of fossils, use of diesel engines). Most of these activities release heavy metals into the environment which end up in the aquatic systems. Heavy metal pollution is a serious environmental issue and can adversely affect humans, animals, plants, and microbes [81]. Even at very low concentrations, heavy metals are toxic to organisms that inhabit the aquatic ecosystem. The effects of heavy metals in the aquatic systems can range from causing a significant histopathological alteration in fishes to high mortality rates of all aquatic organisms in cases of very high heavy metal concentrations.

There are several sources by which aquatic ecosystems can be contaminated as earlier mentioned but one of the major sources of heavy metal release into water bodies is via effluents from mining operations [82]. Different industrial effluents, agricultural run-offs, and sewage from residential areas have all been reported as sources of heavy metal contamination in water bodies with the discharge of untreated effluents from industries ranking as the foremost source of heavy metal pollution in both groundwater and surface

water. Heavy metal pollution of water bodies is a global issue due to the metals' toxicity, persistence in the environment, bioaccumulation, and biomagnification in food chains [60]. Most rivers, especially those that flow through mining and industrial areas are majorly polluted. This water from the polluted rivers then flows down into the sea and can further sink to the sea bottom as a result of a slowing of the tide. Since the solubility of metals is mainly determined by the water or solvent pH, when there is a rise in the acidity of river water, the ability of the metals to solubilize decreases, and thus they are precipitated towards the sea and can cause more harm to the organisms in these habitats [81].

### **Heavy metal effects on sediments**

Several physicochemical parameters such as salinity, redox state, temperature, particle size, hydrodynamic conditions, microbial content, and organic matter can affect the concentration, adsorption, and desorption of metals in sediments. In this environment, heavy metal distribution is influenced by the total organic matter content, grain size, and sediment chemical composition [83]. The bioavailability of heavy metals in sediments is greatly affected by the pH and thus a decrease in the pH of the sediment can highly increase the competition for binding sites between metal ions and  $H^+$  in the sediments. This may result in the breakdown of metal complexes and thereby free metal ions are released into the water columns. Heavy metal contamination of sediments is a major environmental concern that has ramifications for aquatic organisms as well as human health. In most aquatic ecosystems, sediments can act as the major source of heavy metal contamination, and thus the quality of sediments may reveal how contaminated a water body is. According to Sanyal *et al.* [84], continuous introduction of heavy metals or heavy metal-containing compounds in sediments can adversely affect groundwater through leaching. Also, since heavy metals can sink into the bottom of rivers, a high concentration of heavy metals in riverine sediments poses ecological risks to bottom-dwelling species (benthos).

### **Effect of heavy metal contamination on soils**

Heavy metals and metalloids enter soils from a variety of anthropogenic and lithogenic sources [85]. Smelting and mining activities emit localized pollution into the atmosphere, which eventually settles on the land. The presence and distribution of heavy metals in soils are influenced by factors such as the composition of the parent rock, climatic circumstances, biological, chemical, and physical characteristics of the soil, and the degree of rock weathering. Soils that receive more chemical fertilizers and heavy metal-containing pesticides showed considerable enrichment of heavy metals when compared to soils with minimal or no inputs [83, 84, 85]. Because of the substantial amount of automotive activity on roadways, utilization of diesel engines for power generation, and other industry-based

activities, heavy metal pollution of soils occurs significantly in urban areas. Heavy metal bioavailability in soils is critical for their fate in the environment and uptake by plants. Different heavy metals have varying bio availabilities in soils due to metal speciation as well as soil physicochemical factors. Heavy metals such as zinc, cadmium, copper, lead, and chromium have been identified in significant concentrations in the soil of agricultural lands [86]. Some regions where smelting occurs lack the inhabitation of living organisms such as earthworms (which play a major role in the decomposition of organic matter) and vegetation.

The public health risk posed by heavy metal contamination through the food chain to humans starts from the soil. Heavy metal uptake from the soil into plants through the roots is a potential concern as it leads to bioaccumulation along the food chain, a major threat to animal and human health. In addition, heavy metal contamination in the soil can lead to delayed seed germination, yield depression, chlorosis, reduced nutrient uptake, weak plant growth, disorders in plant metabolism and may also cause inability for biological nitrogen fixation [87]. Heavy metal pollution not only results in adverse effects on various parameters relating to plant quality and yield but also causes changes in the size, composition, and activity of the soil microbial community which are responsible for ecosystem functioning. It is worthy to note that, metals are more tightly linked to soil if the pH, clay content, and organic matter are higher than normal levels [88].

### **Effect of heavy metal contamination on soil microorganisms**

Heavy metals have a direct and indirect impact on microorganisms, which is why they are the first biota to be affected. Metals such as Fe, Zn, Cu, Ni, and Co are essential for certain microbial functions such as metabolism and redox reactions and are therefore required in very minute concentrations. Microorganisms are responsible for a number of soil biochemical reactions responsible for soil quality maintenance, decomposition of xenobiotics, formation of soil organic matter, and generally support ecosystem functioning. Heavy metals in high concentrations can have inhibitory or even toxic effects on living organisms such as reduced soil enzymatic activity and reduced rate of soil respiration [89]. Reports have shown that the release of CO<sub>2</sub> in the soil is proportional to the concentration of heavy metals present. Low concentrations of heavy metals in soil are conducive to the release of CO<sub>2</sub>, while high concentrations of heavy metal pollution conditions significantly inhibit soil respiration [90].

Microorganisms respond differently to heavy metal contamination. Rajapaksha *et al.* [91] conducted an experiment to compare the reactions of fungi and bacteria to different toxic

metals such as zinc and copper in soils and observed that the bacterial population responded more to the increase in heavy metal concentrations in the soils than the fungal species [92]. Some of the deleterious impacts of heavy metals on soil microbial communities have been reported. According to Fashola *et al.* [93], heavy metals like cadmium (Cd) and lead (Pb) have a negative impact on microorganisms which may range from causing cell membrane damage to complete DNA structural destruction. Heavy metals alter the shape, metabolism, and growth of microorganisms by altering the nucleic acid structure, functional disruption, cell membrane disturbance, and reduction in enzyme activity, among other effects. Furthermore, toxic concentrations of heavy metals may cause enzyme damage and, as a result, inactivation of cells [87].

Heavy metals can also change the structure of proteins and nucleic acids, resulting in complexes that are rendered inert. Their effects cause a disruption of the integrity of the microbial cell membranes and can further cause the destruction of the whole cell. Heavy metals can also bind to important metabolites and produce precipitates or chelates [50]. Chromium (Cr) and cadmium (Cd) for example have been shown to cause microbial denaturation and oxidative damage, as well as reduce the activity of heavy metal-resistant bacteria's ability to tolerate or remediate these heavy metals. Chromium (Cr) also can change the structure and function of enzymes by interacting with their carboxyl and thiol groups while subcellular cationic chromium complexes bind electrostatically with negatively charged phosphate groups on DNA, inhibiting replication and perhaps causing mutation [93].

Various metals may have different impacts on different microbiota, and the repercussions may vary depending on whether metal limit amounts in the environment were surpassed. Li *et al.* [94] conducted a study which showed that bacterial responses to heavy metals vary. From their finding, *Acidobacteria\_Gp* and *Proteobacteria thiobacillus*, were positively correlated with Cd, while other bacteria, e.g., *Longilinea, Gp2* and *Gp4*, were negatively correlated with Cd. Also, varying concentrations of heavy metal have different effects on microbial community. Mercury (Hg) for example at high concentrations causes severe losses of diversity and shift in microbial community structures, whereas at low concentration microbial diversity increases [95, 96].

Based on myriads of literature, it is an established fact that microorganisms play diverse and critical roles in the transformation and circulation of heavy metals and other essential elements in the environment. In the nitrogen cycle, which is a very essential biogeochemical process that produces nitrogen in an absorbable form for plant uptake, microorganisms are actively responsible in all four steps of the cycling process. These various processes can be disrupted as a result of heavy metal contamination. For instance, microorganisms involved in nitrification and mineralization of protein molecules are affected by copper pollution of

soils [54]. Also, high concentration of zinc in soils have been reported to inhibit nitrification process and other microbiological processes in soils. In another study, it was reported that concentration of up to 10 ppm of mercury have a toxic effect on nitrogen fixing bacteria in soils [97]. An increase in the concentration of lead in soil surfaces has also been documented to have a negative effect on soils microflora and this can consequently influence the decomposition of organic matter, inhibit microbial enzymatic activities and thus cause soil degradation [92].

Studies have indicated that long term pollution of soils as a result of heavy metal contamination can have severe effect on the microbial population and abundance, microbial quality, quantity and diversity in the soil. In an experiment by Juwakar *et al.*, [98] the abundance of selected microbes in heavy metal spiked and natural soils were compared and it was observed that the microbial groups in the natural soils were more abundant than in the spiked soils. In another experiment by Lernat and Wolny-Koladka [99] contaminated and uncontaminated heavy metal polluted soils of Arcelor Mittal steelworks in Cracow were analyzed and the results indicated that there was relative abundance of soil bacteria present in the uncontaminated soils as compared to heavy metal polluted soils. Heavy metal contamination in soils can cause a significant reduction in the diversity and population of microorganisms which can further lead to a reduction in microbial biomass and selective enrichment. Soil exposure to heavy metal contamination has also led to the establishment of heavy metal tolerant microorganisms which can be applied in the bioremediation of heavy metal polluted environments. Some of the known heavy metal resistant bacteria include representations from gram-negative bacteria such as *Alcaligenes*, *Pseudomonas*, *Burkholderia* and gram-positive bacteria such as *Bacillus*, *Corynebacterium*, and *Arthrobacter* [100, 101]

### **Microbial resistance to heavy metal and bioremediation**

Heavy metals hinder microbial growth by blocking necessary functional groups or interfering with the integration of important metal ions into biological components. With its high electrostatic attraction and binding affinities to comparable sites, heavy metal disrupts the binding of important metal ions to the cellular structure [102] which results in destabilization of structure and biomolecules (cell wall enzymes, DNA, RNA), replication errors, and mutagenesis. Heavy metal pollution alters the soil microbial community composition resulting in selective enrichment whereby microorganisms capable of adapting, tolerating, and resisting this stressor increase in abundance. These groups of organisms are referred to as heavy metal resistant microbial strains which have been identified and documented to possess genetic capabilities to resist and tolerate heavy metal contamination in the environment through different mechanisms. These mechanisms include the

production of extracellular polysaccharides that binds and immobilizes toxic metals, biosorption mechanisms, changes in redox potential, sequestration, chelation, and methylation of metals [103].

Microbial cells are capable of preventing metal intoxication by releasing metal-binding compounds into the surroundings. Fungi and bacterial species which are able to produce melanin, a secondary metabolite with strong ion chelation properties can also help to keep metals outside the cells of the organisms. Many soil microorganisms, such as the common fungus *Aspergillus niger*, solubilize metals by releasing organic acids or by immobilizing metals through the excretion of various chemicals, such as oxalates [104].

Plant-associated microbes such as rhizospheric microbes (plant growth promoting rhizobacteria, PGPR), endophytic microbes, and arbuscular mycorrhizal fungi have the ability to alter the bioavailability of heavy metals through the production of chelating agents, the release of acids, phosphate solubilization and changes in redox potential [105]. Kushwaha *et al.* [106] have reported the action of *P. fluorescens* and *Alcaligenes faecalis* in the oxidation of chromium VI to III and As to AsV. The rhizospheric soil which is the soil surrounding the root region of the plant is rich in microbial diversity and population as a result of the exudates released by the plant in this environment which contains substances necessary for microbial growth. This region is known to influence the availability and mobility of heavy metals to plants through the action of microorganisms which consequently promote the removal of heavy metals from the environment through a process known as rhizoremediation or phytoremediation. The PGPR supplement plant growth through various mechanisms which improves nutrient uptake and stimulates plant development.

Also, plant exposure to heavy metals activates the induction of several defense responses such as compartmentalization of the complexed metal ions, immobilization, exclusion, and the expression of stress-responsive proteins and hormones [107]. The presence of plant-associated microbes increases the potential and efficiency of plants to remediate heavy metals from the environment. This class of microorganisms possesses traits such as mineral solubilization, nitrogen fixation, siderophore production, phytohormone production, heavy metal stress tolerance and tolerance to other abiotic stresses, and biocontrol abilities. Therefore, plant-microbe interactions make the process of phytoremediation more efficient. Plants provide the carbon source for microbial growth which on the other hand remove the heavy metal due to their metabolic activity. Also, mycorrhizal fungi are known to enhance the efficiency of the phytoremediation process by providing a large absorption surface area to plants to increase water and nutrient uptake. In addition, they help to prevent bioaccumulation of heavy metals in plants by creating an exclusion barrier for better plant

survival in a heavy metal polluted environment. This is one of the most promising methods for remediation of the metalliferous environment, safe agricultural practices, and improved microbes-mediated metal tolerance [105]. In recent times, genetically engineered microbes are being widely exploited and explored to enhance the amelioration of HMs and to increase stress tolerance in plants in a process referred to as the “novel phytomicrobial strategy” [108].

## Conclusion

Environmental pollution by heavy metals is a global menace with consequences transcending beyond abiotic to biotic. Most of the biotic components play significant roles in driving ecosystem functions and balance. This study has extensively analyzed and highlighted the fate of heavy metals in the environment with special reference to the soil environment and its possible roles in supporting biological entities and mediating certain biochemical processes at low or permissible limits. It has been revealed that HM at high concentrations is highly toxic and could disrupt the metabolic function and activities of microbes as well as damage soil structure and integrity. Also, possible mechanisms have been designed to remediate and decontaminate HM polluted environment and in recent times, the integrated system of plant-microbe interaction has been applied in a technology known as phytoremediation. More recently, biotechnological studies have been applied in genetically modifying microorganisms with the selective advantage of HM resistance to promote phytoremediation of HM more efficiently. Despite the successes gained in the application of this technology, more research is required to improve the activities of microorganisms to be HM-specific and to facilitate removal within the shortest time duration.

## References

1. Zhang, X.; Yan, L.; Liu, J.; Zhang, Z.; Tan, C. (2019). Removal of different kinds of heavy metals by novel PPG-nZVI beads and their application in simulated stormwater infiltration facility. *Appl. Sci.* 9 4213.
2. Duruibe J., Ogwuegbu M., Egwurugwu J. (2007). Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences*, 2(5):112–118.
3. Shrestha R, Ban S, Devkota S, Sharma S, Joshi R, Tiwari AP, Kim HY, Joshi MK. (2021). Technological trends in heavy metals removal from industrial wastewater: A review. *Journal of Environmental Chemical Engineering*. (4):105688.
4. Duffus, Y., Jiang, Y., Huang, H., Mou, L., Ru, J., Zhao, J., et al., (2012). Long-term and high-concentration heavy-metal contamination strongly influences the

- microbiome and functional genes in Yellow River sediments. *Sci. Total Environ.* 637–638, 1400–1412.
5. Bruins, M.R.; Kapil, S.; Oehme, F.W. (2016). Microbial resistance to metals in the environment. *Ecotoxicol. Environ.*, 45, 198–207.
  6. Concas, A.; Arda, C.; Cristini, A.; Zuddas, P.; Cao, G. (2006). Mobility of heavy metals from tailings to stream waters in a mining activity contaminated site. *Int. J. Environ.*, 63, 244–253.
  7. US Environmental Protection Agency (USEPA) (2020). US Environmental Protection Agency (USEPA) Integrated Risk Information System of the US Environmental Protection Agency; USEPA: Washington, DC, USA, 2020.
  8. Gati J, Kosobucki P., Kowalkowski T. and Buszewsk B., (2016). Influence of clinoptilolite rock on chemical speciation of selected heavy metals in sewage sludge. *Journal of Hazardous Materials*,149, 310–316.
  9. Hamelink JL, Landrum PF, Harold BL, William BH, editors. (1994). *Bioavailability: Physical, Chemical, and Biological Interactions*. Boca Raton, FL: CRC Press Inc.
  10. Lasota J, Błońska E, Lyszczarz S, et al. (2020). Forest humus type governs heavy metal accumulation in specific organic matter fractions. *Water, Air & Soil pollution*.231:80.
  11. D'amore, J.; Al-Abed, S.; Scheckel, K.; Ryan, J. (2005). Methods for speciation of metals in soils. *J. Environ. Qual.*, 34, 1707–1745.
  12. Kagel, A., Bates, D., Gawell, K., 2005. *A Guide to Geothermal Energy and the Environment*. Geothermal Energy Association, Washington, DC, pp. 75.
  13. Nelson, S.M., Fielding, E.J., Zamora-Arroyo, F., Flessa, K., 2013. Delta dynamics: effects of a major earthquake, tides, and river flows on Ciénega de Santa Clara and the Colorado River delta, Mexico. *Ecol. Eng.* 59, 144–156.
  14. Maxwell, O., Idoko, F. E., Ologunorisa, T. and Okoya, A. (2012). Temporal Variability of Heavy Metals Concentration in Rural Groundwater of Benue State, Middle Belt, Nigeria. *Journal of Sustainable Development*. 5. 10.5539/jsd.v5n2p2.
  15. Turpeinen, R. (2002). Interactions between Metals, Microbes and Plants: Bioremediation of Arsenic and Lead Contaminated Soils. 258–266.
  16. Smejkalova, M., O. Mikanova, and L. J. P. S. Boruvka. "Effects of heavy metal concentrations on biological activity of soil micro-organisms." *Plant Soil and Environment* 49.7 (2003): 321-326.
  17. Chakravarty, Rajdeep, and Pataki C. Banerjee. "Morphological changes in an acidophilic bacterium induced by heavy metals." *Extremophiles* 12.2 (2008): 279-284.

18. Ndeddy Aka, R.J.; Babalola, O.O. (2016). Effect of bacterial inoculation of strains of *Pseudomonas aeruginosa*, *Alcaligenes faecalis* and *Bacillus subtilis* on germination, growth and heavy metal (Cd, Cr, and Ni) uptake of *Brassica juncea*. *Int. J. Phytoremed*, 18, 200–209.
19. Dubey RK, Tripathi V, Prabha R, et al. (2020). Methods for exploring soil microbial diversity. In: *Unravelling the Soil Microbiome*. SpringerBriefs in Environmental Science. Cham (Switzerland): Springer; 23–32.
20. Ndeddy Aka, R.J.; Babalola, O.O. (2016). Effect of bacterial inoculation of strains of *Pseudomonas aeruginosa*, *Alcaligenes faecalis* and *Bacillus subtilis* on germination, growth and heavy metal (Cd, Cr, and Ni) uptake of *Brassica juncea*. *Int. J. Phytoremed*, 18, 200–209.
21. Ricachenevsky, F. K., Menguer, P. K., Sperotto, R. A., Williams, L. E., & Fett, J. P. (2013). Roles of plant metal tolerance proteins (MTP) in metal storage and potential use in biofortification strategies. *Frontiers in plant science*, 4, 144.
22. Singh Samiksha, Parihar Parul, Singh Rachana, Singh Vijay P., Prasad Sheo M. 2016. Heavy Metal Tolerance in Plants: Role of Transcriptomics, Proteomics, Metabolomics, and Ionomics. *Frontiers in Plant Science*. 6: DOI=10.3389/fpls.2015.01143.
23. Fidalgo, F., Azenha, M., Silva, A. F., de Sousa, A., Santiago, A., Ferraz, P., & Teixeira, J. (2013). Copper-induced stress in *Solanum nigrum* L. and antioxidant defense system responses. *Food and Energy Security*, 2(1), 70-80.
24. Wuana R. A., Okieimen, F. E. "Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation", *International Scholarly Research Notices*, vol. 2011, Article ID 402647, 20 pages, 2011. <https://doi.org/10.5402/2011/402647>.
25. Nandakumar PBA, Dushenkov V, Motto H, Raskin I, 1995. Phytoextraction: The use of plants to remove heavy metals from soils. *Environ. Sci. Technol.* 29:1232-1238.
26. Yang, X., Feng, Y., He, Z., & Stoffella, P. J. (2005). Molecular mechanisms of heavy metal hyperaccumulation and phytoremediation. *Journal of trace elements in medicine and biology*, 18(4), 339-353.
27. Xie, Y.; Fan, J.; Zhu, W.; Amombo, E.; Lou, Y.; Chen, L.; Fu, J. (2016). Effect of heavy metals pollution on soil microbial diversity and Bermudagrass genetic variation. *Front. Plant Sci*, 7,755.
28. Bajkic´, S.; Naranc´ic´, T.; Đokic´, L.; Đord´evic´, D.; Nikodinovic´-Runic´, J.; Moric´, I.; Vasiljevic´, B. (2013). Microbial diversity and isolation of multiple metal-tolerant bacteria from surface and underground pits within the copper mining and smelting complex bor. *Arch. Biol. Sci*, 65, 375–386.

29. Yao, J.; Tian, L.; Wang, Y.; Djah, A.; Wang, F.; Chen, H.; Su, C.; Zhuang, R.; Zhou, Y.; Choi, M.M.F.; et al. (2008). Microcalorimetric study the toxic effect of hexavalent chromium on microbial activity of Wuhan brown sandy soil. *Ecotoxicol. Environ. Saf*, 69, 89–95.
30. Alirzayeva, Esmira G., et al. "Heavy metal accumulation in *Artemisia* and foliaceous lichen species from the Azerbaijan flora." *Forest snow and landscape research* 80.3 (2006): 339-348.
31. Lenart, A., & Wolny-Koładka, K. (2013). The effect of heavy metal concentration and soil pH on the abundance of selected microbial groups within ArcelorMittal Poland steelworks in Cracow. *Bulletin of Environmental Contamination and toxicology*, 90(1), 85-90.
32. Cullen, J. T., & Maldonado, M. T. (2013). Biogeochemistry of cadmium and its release to the environment. *Cadmium: from toxicity to essentiality*, 31-62.
33. Khan, F. I., Husain, T., & Hejazi, R. (2004). An overview and analysis of site remediation technologies. *Journal of environmental management*, 71(2), 95-122.
34. Annan, E., Agyei-Tuffour, B., Bensah, Y. D., Konadu, D. S., Yaya, A., Onwona-Agyeman, B., & Nyankson, E. (2018). Application of clay ceramics and nanotechnology in water treatment: A review. *Cogent Engineering*, 5(1), 1476017.
35. El-Gohary, F. A. "A historical perspective on the development of water supply in Egypt." *Evolution of WatEr Supply through thE MillEnnia* (2019): 127.
36. Dube, R. K. (2006). The extraction of lead from its ores by the iron-reduction process: A historical perspective. *JOM*, 58(10), 18-23.
37. Levin, R., Vieira, C. L. Z., Rosenbaum, M. H., Bischoff, K., Mordarski, D. C., & Brown, M. J. (2021). The urban lead (Pb) burden in humans, animals and the natural environment. *Environmental research*, 193, 110377.
38. Jyothi, N. R. (2020). Heavy metal sources and their effects on human health. *Heavy Metals-Their Environmental Impacts and Mitigation*.
39. Mohammadyan, M., Moosazadeh, M., Borji, A., Khanjani, N., & Rahimi Moghadam, S. (2019). Investigation of occupational exposure to lead and its relation with blood lead levels in electrical solderers. *Environmental monitoring and assessment*, 191(3), 1-9.
40. Wildemann, T. M., Siciliano, S. D., & Weber, L. P. (2016). The mechanisms associated with the development of hypertension after exposure to lead, mercury species or their mixtures differs with the metal and the mixture ratio. *Toxicology*, 339, 1-8.
41. Sengar, R. S., Gautam, M., Sengar, R. S., Garg, S. K., Sengar, K., & Chaudhary, R. (2008). Lead stress effects on physiobiochemical activities of higher plants. *Reviews of Environmental Contamination and Toxicology Vol 196*, 73-93

42. Lepp, Nicholas W., ed. Effect of heavy metal pollution on plants: metals in the environment. Vol. 2. Springer Science & Business Media, 2012.
43. ATSDR, U. (1995). Department of Health and Human Services. ATSDR/EPA Priority List.
44. Adhikari, S., Yanuar, E., & Ng, D. Q. (2022). Widespread nickel contamination in drinking water supplies of elementary schools in Taichung, Taiwan. *Environmental Science and Pollution Research*, 29(9), 12531-12539.
45. Kasprzak, K. S., Diwan, B. A., Kaczmarek, M. Z., Logsdon, D. L., Fivash, M. J., & Salnikow, K. (2011). Effects of ascorbic acid on carcinogenicity and acute toxicity of nickel subsulfide, and on tumor transplants growth in gulonolactone oxidase knock-out mice and wild-type C57BL mice. *Toxicology and applied pharmacology*, 257(1), 32-37.
46. Nieminen TM, Ukonmaanaho L, Rausch N, Shotyk W. In: Metal Ions in Life Sciences. Sigel A, Sigel H, Sigel RKO, editors. Vol. 2. John Wiley & Sons, Ltd; New York, NY: 2007. pp. 1–30.
47. Meija, J., Coplen, T. B., Berglund, M., Brand, W. A., De Bièvre, P., Gröning, M., ... & Prohaska, T. (2016). Isotopic compositions of the elements 2013 (IUPAC Technical Report). *Pure and Applied Chemistry*, 88(3), 293-306.
48. Hemond, H. F., & Fechner, E. J. (2014). Chemical fate and transport in the environment. Elsevier.
49. Fallah, A., Mohammad-Hasani, A., & Colagar, A. H. (2018). Zinc is an essential element for male fertility: a review of Zn roles in men's health, germination, sperm quality, and fertilization. *Journal of reproduction & infertility*, 19(2), 69.
50. Zhang, T., Wang, W., Zhao, Y., Bai, H., Wen, T., Kang, S., ... & Komarneni, S. (2021). Removal of heavy metals and dyes by clay-based adsorbents: From natural clays to 1D and 2D nano-composites. *Chemical Engineering Journal*, 420, 127574.
51. Hambidge, M. (2003). Biomarkers of trace mineral intake and status. *The Journal of nutrition*, 133(3), 948S-955S.
52. Sagardoy, R. U. T. H., Morales, F. E. R. M., López Millán, A. F., Abadía, A. N. U. N. C. I. A. C. I. Ó. N., & Abadía, J. A. V. I. E. R. (2009). Effects of zinc toxicity on sugar beet (*Beta vulgaris* L.) plants grown in hydroponics. *Plant Biology*, 11(3), 339-350.
53. Wei, X., Desai, D., Yadav, G. G., Turney, D. E., Couzis, A., & Banerjee, S. (2016). Impact of anode substrates on electrodeposited zinc over cycling in zinc-anode rechargeable alkaline batteries. *Electrochimica Acta*, 212, 603-613.
54. Nevzorova T., and Kutcherov, V. (2019). Barriers to the wider implementation of biogas as a source

- of energy: A state-of-the-art review, *Energy Strategy Reviews*, Volume 26, 100414, doi.org/10.1016/j.esr.2019.100414.
55. Vincent M, Hartemann P, Engels-Deutsch M. Antimicrobial applications of copper. *Int J Hyg Environ Health*. 2016 Oct;219(7 Pt A):585-591. doi: 10.1016/j.ijheh.2016.06.003. Epub 2016 Jun 3. PMID: 27318723.
  56. Tsai, M.-T., Huang, S.-Y., and Cheng, S.-Y. (2017). Lead poisoning can be easily misdiagnosed as acute porphyria and nonspecific abdominal pain Case reports in emergency medicine 2017. *Case Rep. Emerg Med*. 2017 (2), 1–4. doi:10.3109/10408444.2013.768596
  57. Gautam, P. K., Gautam, R. K., Banerjee, S., Chattopadhyaya, M. C., & Pandey, J. D. (2016). Heavy metals in the environment: fate, transport, toxicity and remediation technologies. Nova Sci Publishers, 60, 101-130.
  58. Yang Y, Chang AC, Wang M, Chen W, Peng C. Assessing cadmium exposure risks of vegetables with plant uptake factor and soil property. *Environ Pollut*. 2018;238: 263–269. doi: 10.1016/j.envpol.2018.02.059
  59. Walker, C. H., Sibly, R. M., & Peakall, D. B. (2005). *Principles of ecotoxicology*. CRC press.
  60. Chen, Q., Tao, Y., Zhang, Q., & Qi, C. (2022). The rheological, mechanical and heavy metal leaching properties of cemented paste backfill under the influence of anionic polyacrylamide. *Chemosphere*, 286, 131630.
  61. Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., & Sutton, D. J. (2012). Heavy metal toxicity and the environment. *Molecular, clinical and environmental toxicology*, 133-164.
  62. Slaveykova, V. I., & Cheloni, G. (2018). Preface: special issue on environmental toxicology of trace metals. *Environments*, 5(12), 138.
  63. Caeiro, S., Costa, M. H., Ramos, T. B., Fernandes, F., Silveira, N., Coimbra, A., ... & Painho, M. (2005). Assessing heavy metal contamination in Sado Estuary sediment: an index analysis approach. *Ecological indicators*, 5(2), 151-169.
  64. Oremland, R. S., & Stolz, J. F. (2003). The ecology of arsenic. *Science*, 300(5621), 939-944.
  65. Mandal, B. K., & Suzuki, K. T. (2002). Arsenic round the world: a review. *Talanta*, 58(1), 201-235.
  66. Garg, N., & Singla, P. (2011). Arsenic toxicity in crop plants: physiological effects and tolerance mechanisms. *Environmental chemistry letters*, 9(3), 303-321.
  67. Dittmar J, Voegelin A, Roberts LC, Hug SJ, Saha GC, Ali MA, Badruzzaman BM, Kretzschmar R (2007) Spatial distribution and temporal variability of arsenic in irrigated rice fields in Bangladesh. 2. Paddy soil. *Environ Sci Technol* 41:5967–5972

68. Panaullah, G. M., Alam, T., Hossain, M. B., Loeppert, R. H., Lauren, J. G., Meisner, C. A., ... & Duxbury, J. M. (2009). Arsenic toxicity to rice (*Oryza sativa* L.) in Bangladesh. *Plant and soil*, 317(1), 31-39.
69. Brzóska, M.M., Moniuszko-Jakoniuk, J., 2001. Interactions between cadmium and zinc in the organism. *Food Chem.Toxicol.* 39, 967–980.
70. Hussain, B., Ashraf, M. N., Abbas, A., Li, J., & Farooq, M. (2021). Cadmium stress in paddy fields: effects of soil conditions and remediation strategies. *Science of The Total Environment*, 754, 142188.
71. Singh, P., Singh, I., Shah, K., 2020. Alterations in antioxidative machinery and growth parameters upon application of nitric oxide donor that reduces detrimental effects of cadmium in rice seedlings with increasing days of growth. *S. Afr. J. Bot.* 131, 283–294.
72. Hasan, S. A., Fariduddin, Q., Ali, B., Hayat, S., & Ahmad, A. (2009). Cadmium: toxicity and tolerance in plants. *J Environ Biol*, 30(2), 165-174.
73. Al Yemens, M.N.: Effect of cadmium, mercury and lead on seed germination and early seedling growth of *Vigna ambacensis* L. *Indian J. Plant Physiol.*, 6, 147-151 (2001)
74. Mitra, S., Pramanik, K., Ghosh, P.K., Soren, T., Sarkar, A., Dey, R.S., Pandey, S., Maiti, T.K., 2018a. Characterization of Cd-resistant *Klebsiella michiganensis* MCC3089 and its potential for rice seedling growth promotion under Cd stress. *Microbiol. Res.* 210, 12–25
75. Afzal, M., Yu, M., Tang, C., Zhang, L., Muhammad, N., Zhao, H., Feng, J., Yu, L., Xu, J., 2019. The negative impact of cadmium on nitrogen transformation processes in a paddy soil is greater under non-flooding than flooding conditions. *Environ. Int.* 129, 451–460
76. Chen, Q., Lu, X., Guo, X., Pan, Y., Yu, B., Tang, Z., Guo, Q., 2018a. Differential responses to Cd stress induced by exogenous application of Cu, Zn or Ca in the medicinal plant *Catharanthus roseus*. *Ecotoxicol. Environ. Saf.* 157, 266–275.
77. Huybrechts, M., Hendrix, S., Bertels, J., Beemster, G.T.S., Vandamme, D., Cuypers, A., 2020. Spatial analysis of the rice leaf growth zone under controlled and cadmium-exposed conditions. *Environ. Exp. Bot.* 177, 104120.
78. Islam, M. S., Khanam, M. S., & Sarker, N. I. (2018). Health risk assessment of metals transfer from soil to the edible part of some vegetables grown in Patuakhali province of Bangladesh. *Arc Agri Environ Sci*, 3(2), 187-97.
79. Rezania, S., Taib, S. M., Din, M. F. M., Dahalan, F. A., & Kamyab, H. (2016). Comprehensive review on phytotechnology: heavy metals removal by diverse aquatic plants species from wastewater. *Journal of hazardous materials*, 318, 587-599.

80. Zhuang, W., & Gao, X. (2014). Assessment of heavy metal impact on sediment quality of the Xiaoqinghe estuary in the coastal Laizhou Bay, Bohai Sea: Inconsistency between two commonly used criteria. *Marine pollution bulletin*, 83(1), 352-357.
81. Rajaei, G., Mansouri, B., Jahantigh, H., & Hamidian, A. H. (2012). Metal concentrations in the water of Chah nimeh reservoirs in Zabol, Iran. *Bulletin of environmental contamination and toxicology*, 89(3), 495-500.
82. Ali, H., & Khan, E. (2018). Bioaccumulation of non-essential hazardous heavy metals and metalloids in freshwater fish. Risk to human health. *Environmental chemistry letters*, 16(3), 903-917.
83. Islam, M. S., Ahmed, M. K., Raknuzzaman, M., Habibullah-Al-Mamun, M., & Islam, M. K. (2015). Heavy metal pollution in surface water and sediment: a preliminary assessment of an urban river in a developing country. *Ecological indicators*, 48, 282-291.
84. Sanyal, T., Kaviraj, A., & Saha, S. (2015). Deposition of chromium in aquatic ecosystem from effluents of handloom textile industries in Ranaghat–Fulia region of West Bengal, India. *Journal of advanced research*, 6(6), 995-1002.
85. Alloway, B. J. (2013). Sources of heavy metals and metalloids in soils. In *Heavy metals in soils* (pp. 11-50). Springer, Dordrecht.
86. Gupta, D. K., Chatterjee, S., Datta, S., Veer, V., & Walther, C. (2014). Role of phosphate fertilizers in heavy metal uptake and detoxification of toxic metals. *Chemosphere*, 108, 134-144.
87. Singh, Dr. Jiwan & Kalamdhad, Ajay. (2011). Effects of Heavy Metals on Soil, Plants, Human Health and Aquatic Life. *International Journal of Research in Chemistry and Environment*. 1. 15-21.
88. Chibuike, G. U., & Obiora, S. C. (2014). Heavy metal polluted soils: effect on plants and bioremediation methods. *Applied and environmental soil science*, 2014.
89. Chen, X., Zhao, Y., Zhang, C., Zhang, D., Yao, C., Meng, Q., & Wei, Z. (2020). Speciation, toxicity mechanism and remediation ways of heavy metals during composting: A novel theoretical microbial remediation method is proposed. *Journal of Environmental Management*, 272, 111109.
90. Chu, D. (2018). IOP Conf. Series: Earth and Environmental Science 113 (2018) 012009 doi :10.1088/1755-1315/113/1/012009 Effects of heavy metals on soil microbial community
91. Rajapaksha, R. D. A. A., Hashim, U., Uda, A., Fernando, C. A. N., & De Silva, S. N. T. (2017). Target ssDNA detection of *E. coli* O157: H7 through electrical based DNA biosensor. *Microsystem Technologies*, 23(12), 5771-5780.

92. Georgopoulos, P., Yonone-Lioy, M., Opiekun, R. and Lioy, P. (2001). Environmental copper: Its dynamics and human exposure issues. *Journal of toxicology and environmental health. Part B, Critical reviews.* 4. 341-94. 10.1080/109374001753146207.
93. Fashola, M. O., Ngole-Jeme, V. M., & Babalola, O. O. (2016). Heavy metal pollution from gold mines: environmental effects and bacterial strategies for resistance. *International journal of environmental research and public health*, 13(11), 1047.
94. Li X, Meng D, Li J, Yin H, Liu H, Liu X, et al. Response of soil microbial communities and microbial interactions to long-term heavy metal contamination. *Environ Pollut.* 2017;231: 908–917. doi: 10.1016/j.envpol.2017.08.057.
95. Rai PK, Lee SS, Zhang M, Tsang YF, Kim KH. Heavy metals in food crops: health risks, fate, mechanisms, and management. *Environ Int.* 2019;125: 365–385. doi: 10.1016/j.envint.2019.01.067
96. Yang Y, Chang AC, Wang M, Chen W, Peng C. Assessing cadmium exposure risks of vegetables with plant uptake factor and soil property. *Environ Pollut.* 2018;238: 263–269. doi: 10.1016/j.envpol.2018.02.059
97. Schwarz, K., Pickett, S. T., Lathrop, R. G., Weathers, K. C., Pouyat, R. V., & Cadenasso, M. L. (2012). The effects of the urban built environment on the spatial distribution of lead in residential soils. *Environmental pollution*, 163, 32-39.
98. Juwarkar, A. A., Nair, A., Dubey, K. V., Singh, S. K., & Devotta, S. (2007). Biosurfactant technology for remediation of cadmium and lead contaminated soils. *Chemosphere*, 68(10), 1996-2002.
99. Lenart, A., & Wolny-Koładka, K. (2013). The effect of heavy metal concentration and soil pH on the abundance of selected microbial groups within ArcelorMittal Poland steelworks in Cracow. *Bulletin of Environmental Contamination and toxicology*, 90(1), 85-90.
100. Fakhar, A., Gul, B., Gurmani, A. R., Khan, S. M., Ali, S., Sultan, T., ... & Rizwan, M. (2022). Heavy metal remediation and resistance mechanism of *Aeromonas*, *Bacillus*, and *Pseudomonas*: A review. *Critical Reviews in Environmental Science and Technology*, 52(11), 1868-1914.
101. Pal, A., Bhattacharjee, S., Saha, J., Sarkar, M., & Mandal, P. (2022). Bacterial survival strategies and responses under heavy metal stress: A comprehensive overview. *Critical Reviews in Microbiology*, 48(3), 327-355.
102. Balali-Mood Mahdi, Naseri Kobra, Tahergorabi Zoya, Khazdair Mohammad Reza, Sadeghi Mahmood. (2021). Toxic Mechanisms of Five Heavy Metals: Mercury, Lead, Chromium, Cadmium, and Arsenic. *Frontiers in Pharmacology*. 12: DOI=10.3389/fphar.2021.643972

103. Gomathy, M., & Sabarinathan, K. G. (2010). Microbial mechanisms of heavy metal tolerance-A review. *Agricultural Reviews*, 31(2).
104. Bahaloo-Horeh, N., & Mousavi, S. M. (2017). Enhanced recovery of valuable metals from spent lithium-ion batteries through optimization of organic acids produced by *Aspergillus niger*. *Waste management*, 60, 666-679.
105. Mishra, J., Singh, R. & Arora, N. K. (2017). Alleviation of heavy metal stress in plants and remediation of soil by rhizosphere microorganisms. *Frontiers in Microbiology*, 8, 1706.
106. Kushwaha, A., Rani, R., Kumar, S. & Gautam, A. (2015). Heavy metal detoxification and tolerance mechanisms in plants: Implications for phytoremediation. *Environmental Reviews*, 24(1), 39–51.
107. Chauhan, R., Awasthi, S., Indoliya, Y., Chauhan, A. S., Mishra, S., Agrawal, L., Srivastava, S., Dwivedi, S., Singh, P. C., Mallick, S., Chauhan, P. S., Pande, V., Chakrabarty, D. & Tripathi, R. D. (2020). Transcriptome and proteome analyses reveal selenium mediated amelioration of arsenic toxicity in rice (*Oryza sativa* L.). *J Hazard Mat* 390:122122
108. Arora, N. K. and Chauhan, R. (2021). Heavy metal toxicity and sustainable interventions for their decontamination. *Environmental Sustainability*, 4, 1–3 <https://doi.org/10.1007/s42398-021-00164-y>