

## **Review Article**

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

#### **ABSTRACT**

The environment comprises of biotic and abiotic components interacting as a system. The environment contains organic and inorganic minerals in 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 HM are biologically essential elements required in the body/plant or as constituents of important enzymes although in trace amounts while others are non-essential which 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 metal 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 were analysed 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 < 10ppm 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. Other industrial sources of heavy metal pollution include combustion of coals and petroleum in power plants, quarry, and metal processing in refineries, nuclear power plants, high-tension lines, plastic, textile and paper processing industries [4].

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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 keys 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 concentration. According to USEPA (USEPA 2020), the limit for HMs in soil and for oral dose 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].

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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 the natural geochemical sport processes through phylogenic activities like mining has led to the accumulation of heavy metals 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 ground water overtime can cause increased accumulation of the metals and thus escalating the concentrations to a level far beyond the acceptable recommendations [14].

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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 the 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 the 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 community, it is important to first identify their structure, abundance and distribution. Additionally, an in-depth knowledge on 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 is 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 in 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, 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 are toxic to plants even at low concentrations. In soil, when HM pollution occurs, it is transported round the soil and its fate is dependent significantly on 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 controls 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 has 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 food chain occurs which can result to 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.

Researches 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. Majority of the studies conducted have used both culture dependent and independent methods to determine the effects of heavy metal contamination on 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 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 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, arbuscular mycorrhizal fungi have the ability to alter the bioavailability of heavy metal through production of chelating agents, release of acids, phosphate solubilization and changes in redox potential [91]. This review therefore captures heavy metal as an environmental pollutant and its 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 Satarug *et al.* [32], 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 of 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, 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 which 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 pollutions in the environment [37].

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Lead is a common contaminant found in soil and unlike other metals it is toxic to biotic elements and has no biological role in the environment. Uptake of lead in food, water and air are the most significant ways by which lead enters into 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 very high level of lead may produce encephalopathy [39]. In most cases, a repetitive or continued exposure to lead can cause a toxic stress on the kidney, which if untreated may result into an irreversible and chronic intestinal nephritis [39]. Lead exposures have also been reported as a major factor which may contribute to the development of hypertension. Wildemann *et al.*, [40] also discovered that an 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 an inhibition in the intracellular physiological processes of the plant. Numerous researches 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, 23 percent decrease in dry weight, and a 26 percent decrease in chlorophyll content. The plant length was also reduced by 34 percent and the root length 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].

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### **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 steels. 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 sea floor 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,  $Zn^{2+}$  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 categorised 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 haemoglobin. 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. It has been reported that there is a complex but defined interaction between copper and the environment [96]. 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].

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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, researches 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 an atomic weight of 200.6, atomic number 80, melting point  $-13.6^{\circ}\text{C}$ , and boiling point  $357^{\circ}\text{C}$ , density  $13.6\text{ g cm}^{-3}$ , and is usually recovered as a byproduct of ore processing. There are several sources of Hg into 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. **The forms of Hg present** different properties and toxicity. 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 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 condition. 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 the 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 lights bulbs in lamp manufacturing companies, 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 [97].

#### **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 the industries, agriculture, medicine and other fields resulting in their dispersion into the environment, including the air, water, and soils. Anthropogenic activities has 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 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, pharmaceutical processes, from farms and even residential areas. These heavy metals can get into the human systems via direct skin contact to 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, 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].

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

Heavy metals contaminate fresh water 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 [64]. 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 has serious consequences for public health [65]. 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 [66].

### **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 water environment results majorly from anthropogenic activities such as agriculture (pesticides, fertilizers), urbanization (deforestation, automotive activities) and industrialization (mining, constructions, refining of fossils, and 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 [67]. 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.

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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 [68]. Different industrial effluents, agricultural run-offs, 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 bio magnification 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 flow down into the sea and can further sink to the sea bottom as a result of 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 [67].

#### **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 the sediment chemical composition [69]. 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.* [70], continuous introduction of heavy metals or heavy metal containing compounds in sediments can adversely affect ground water through leaching. Also, since heavy metals can sink into the bottom of rivers, a high concentration of heavy metal 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 [71]. 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 parent rock, climatic circumstances, biological, chemical and physical characteristics of the soil and the degree of rock weathering. Soils which receive more chemical fertilizers and heavy metal containing pesticides showed considerable enrichment of heavy metals when compared to soils with minimal or no inputs [69, 70, 71]. Because of substantial amount of automotive activity on roadways, utilization of diesel engines for power generation and other industry based activities, heavy metal pollution of soils occur 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 and this is as a result of 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 [72]. 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.

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 metals contamination in 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 [73]. Heavy metal pollution not only result in adverse effects on various parameters relating to plant quality and yield but also cause 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 [74].

### **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, 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 supports 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 [75]. Reports have shown that the release of CO<sub>2</sub> in soil is proportional to the concentration of heavy metal present. Low concentrations of heavy metal in soil are conducive to the release of CO<sub>2</sub>, while high concentrations of heavy metal pollution conditions significantly inhibit soil respiration [76].

Microorganisms respond differently to heavy metal contamination. Rajapaksha *et al.* [77] 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 more than the fungal species [78].

Some of the deleterious impacts of heavy metals on soil microbial communities have been reported. According to Fashola *et al.* [79], 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 through altering nucleic acid structure, functional disruption, cell membranes disturbance, reduction in enzyme activity, among other effects. Furthermore, toxic concentrations of heavy metals may cause enzyme damage and, as a result, inactivation of cells [74].

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 cells membranes and can further cause a 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 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 [79].

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.*, [2017] [80] 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.

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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 [81, 82].

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 has** 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 has** a toxic effect on nitrogen fixing bacteria in soils [83]. 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 [78].

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.*, [84] 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 [85] 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*, *Psuedomonas*, *Burkholderia* and gram-positive bacteria such as *Bacillus*, *Corynebacterium* and *Arthrobacter* [86, 87]

### **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 [88] 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 production of extracellular polysaccharides that binds and immobilizes toxic metals, biosorption mechanisms, and changes in redox potential, sequestration, chelation and methylation of metals [89].

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 excretion of various chemicals, such as oxalates [90].

Plant associated microbes such as rhizospheric microbes (plant growth promoting rhizobacteria, PGPR), endophytic microbes, arbuscular mycorrhizal fungi have the ability to alter the bioavailability of heavy metal through production of chelating agents, release of acids, phosphate solubilization and changes in redox potential [91]. Kushwaha et al. [92] have reported the action of *P. fluorescens* and *Alcaligenes feccalis* in the oxidation of chromium VI to III and As to AsV. The rhizospheric soil which is the soil surrounding the root region of plant is rich in microbial diversity and population as a result of the exudates released by 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 metal 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 response such as compartmentalization of the complexed metal ions, immobilization, exclusion, and the expression of stress responsive proteins and hormones [93]. The presence of plant associated microbes increases the potential and efficiency of plants to remediate heavy metal from the environment. **These classes of microorganisms possess** 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, mycorrhizals are known to enhance the efficiency of the phytoremediation process by providing 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 heavy metal polluted environment. This is one of the most promising methods for remediation of metalliferous environment, for safe agricultural practices and for improved microbes mediated metal tolerance [91]. 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" [94].

## **Conclusion**

Environmental pollution by heavy metal 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 analysed and highlighted the fate of heavy metal in the environment with special reference to 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 are 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 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 on the activities of microorganisms to be HM specific and to facilitate removal within the shortest time duration.

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