Heavy Metals Pollution Of Soil; Toxicity And Phytoremediation Techniques

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Abstract: The rapid industrialization and intensive agricultural activities over the last few decades have resulted in accumulation of various pollutants in the environment, chiefly soil, which has led to the accumulation of heavy metals. The indiscriminate release of heavy metals into the soil and waters is a major health concern worldwide, because of their potential reactivity, toxicity, mobility and as they cannot be broken down to non-toxic forms and therefore has long-lasting effects on the ecosystems. Some metals such as manganese, copper, zinc and nickel are important in very small amounts and beneficial to plants, and animals for their growth and optimum performance, but high concentrations of all these metals have strong toxic effects and pose an environmental threat and causes toxicity in biological systems such as humans, animals, and plants. Many of them are toxic even at very low concentrations and they are not only cytotoxic but also carcinogenic and mutagenic in nature. Source of Contamination of soils with toxic heavy metals through mining operations, discharge of industrial effluents, intensive chemicalization of agriculture based on pesticides, fertilizers, and disinfectant, etc., is of great concern. In order to make the environment healthier for human beings, contaminated soils need to be rectified to make them free from heavy metals. There are some conventional remediation technologies to clean polluted areas, specifically soils contaminated with metals. These methods are expensive, time consuming, and environmentally devastating. Recently, phytoremediation as a cost effective and environmentally friendly technology has been developed in which plants are used to remediate the toxic heavy metals polluted areas, by using specific metallophytes. These plants are known as hyperaccumulators. Phytoremediation is becoming an important tool for decontaminating soil, water, and air by detoxifying, extracting, hyperaccumulating, and/or sequestering contaminants, especially at low levels where, using current methods, costs exceed effectiveness. In this paper, it was reviewed sources, environmental impacts, factors affecting heavy metals bioavailability in plants and phytoremediation techniques of soil heavy metal contamination.

Keywords: Heavy metals, Contamination, Phytoremediation, Hyperaccumulators

1. Introduction

The rapid industrialization and intensive agricultural activities over the last few decades have resulted in accumulation of various pollutants in the environment, chiefly soil and water, which has led to the accumulation of heavy metals and are distributed over wide areas by means of air and water. The environment has been contaminated with organic and inorganic pollutants. A pollutant is any substance in the environment, which causes objectionable effects, impairing the welfare of the environment, reducing the quality of life and may eventually cause death. Hence, environmental pollution is the presence of a pollutant in the environment; air, water and soil, which may be poisonous or toxic and will cause harm to living things in the polluted environment **[1].** Heavy metal contamination of soil is one of the most important environmental problems throughout the world. The ability of heavy metals to accumulate and cause toxicity in biological systems - humans, animals, microorganisms and plants has been reported [2]. Increased the concentration of heavy metals constitute a serious health threat of people and animals. Contamination with heavy metals can affect the whole environment, but the longest-lasting effects occur in the soils, on account of the absorption of many metals on mineral and organic colloids. Metals, unlike other pollutants, remain in the atomic form, although their speciation can change in the time together with changes in the soil conditions. The long-lasting nature of contamination is dependent in the kind of the soil and its physicochemical properties. Removing heavy metals from the soil is a very difficult problem, because they are specific permanent pollution, which can in many causes data pack a few hundred or of even thousands of years [3]. Soil is critically environmental medium, which is subjected to a number of pollutants due to different human activities and it is a complex porous material retains and transports harmful pollutants such as heavy metals into both nearby surface, groundwater and cause a potential risk to human health [4]. It is the fundamental foundation of agricultural resources, food security, global economy and environmental quality. Hence, there is a great need to develop effective technologies for sustainable management and remediation of the contaminated soils [5]. The nature of heavy metals bioaccumulation causes toxicity in biological systems such as humans, animals, microorganisms and plants. Some metals such as manganese, copper, zinc and nickel are important and beneficial to plants, and animals, but high concentrations all these metals have strong toxic effects and pose an environmental threat. Accumulation of heavy metals can reduce soil quality, reduce crop yield and the quality of agricultural products, and thus give negative impacts to the health of human, animals, and the ecosystem [6]. The term heavy metal pollution refers to heavy metal levels that are abnormally high relative to normal background levels and the excessive deposition of toxic heavy metals in the soil caused by human activities [7]. Agencies like the World Health Organization (WHO) and the United states Environment Protection Agency (USEPA) have set stringent standards for maximum permissible limits of heavy metals [8]. Heavy metals, in the environment are a source of concern because of their potential reactivity, toxicity and mobility. The sources of heavy metals in the environment and factors influencing their distribution, reactivity, mobility and toxicity are known to be numerous [9]. Contamination of soils with toxic heavy metals through mining operations, discharge of industrial effluents, intensive chemicalization of agriculture based on pesticides, fertilizers, and disinfectant, etc., is of great concern due to its detrimental effects on soil biological systems and has induced many negative effects on the environmental [10], [11]. It was reported that heavy metals are of considerable environmental concern due to their toxicity, wide sources; they have a long persistence and no biodegradable properties and accumulative behaviors. The half-life of these toxic elements is more than 20 years. According to the United States Environmental Action Group (USEAG), this environmental problem has threatened the health of more than 10 million people in many countries [12]. Although individual metals exhibit specific signs of their toxicity, the following have been reported as general signs associated with Cd, Pb, As, Hg, Zn Cu and Al poisoning: gastrointestinal disorders, diarrhoea, stomatitis, tremor, ataxia, paralysis, vomiting and convulsion, depression, and pneumonia when volatile vapours and fumes are inhaled. The nature of effects could be toxic (acute, chronic or sub-chronic), neurotoxic, carcinogenic, mutagenic or teratogenic [8]. Heavy metals in soil are present in several different forms. The various metal species can be present in a soluble ionic, exchangeable, and organically bound or a residual form. Certain of these forms are more mobile, while other forms are very stable and are not converted readily from one form to another. Different metal fractions within soil require different methods to separate them from the soil matrix. Conventional remediation technologies are based on biological, physical, and chemical methods, which may be used in conjunction with one another to reduce the contamination to a safe and acceptable level. In spite of being efficient, these methods are expensive, time consuming and environmentally destructive. At the same time they are usually harmful to the natural soil environment, and generate large amounts of waste. Recently, phytoremediation, which is an emerging technology, should be considered for remediation of contaminated sites because of its cost effectiveness, aesthetic advantages and long term applicability [13]. Phytoremediation can be defined as “the efficient use of plants to remove, metabolize various molecules in their tissues, detoxify or immobilise environmental contaminants in a growth matrix (soil, water or sediments) through the natural biological, chemical or physical activities and processes of the plants” [14], [15]. Various plant species have been identified and tested for their ability in uptake and accumulation of a variety of different heavy metals as Phytoremediation. To date, more than 400 species have been identified as metal accumulator [16]. Generally, plants show signs of stress when they accumulate high level of heavy metals. Thus, stressed plants may be a sign of metal contamination. However, some plant species are able to accumulate fairly large amounts of heavy metals without showing stress, which represents a potential risk for animals and humans. These plants that easily absorb high levels of metals from the surrounding soil are called hyperaccumulators. Take, for instance, dose of 5-ppm of Cd(II), Cr(VI), Cu(II), Ni(II), and Zn(II) has been reported to promote the root growth of alfalfa plants (Medicago sativa) by 22.0%, 166.0%, 156.0%, 63.0%, and 105.0% respectively. In addition, a dose of 5ppm of Cr(VI), Cu(II), Ni(II), and Zn(II) increased the shoot length in 14.0%, 60.0%, 36.0%, and 7.7%, respectively. A plant is classified as a hyper accumulator for heavy metal (s) when it meets the following criteria; (a) shoot/root quotient > 1, (b) extraction coefficient (level of heavy metal in the shoot divide by total level of heavy metal in the soil) > 1; extraction coefficient gives the proportion of total heavy metal in the soil which is taken up by the plant shoot/aerial part of the plant), (c) Furthermore, a plant which has high levels of heavy metals in the roots but with shoot/root quotients less than 1 is classified as a heavy metal excluder [17]. The aim of this review was to describe plant-soil interactions, to provide a brief view about sources, environmental impacts, factors affecting heavy metals Mobility and Phytoavailability in Plants, phytoremediation strategies of heavy metal contaminated soils and its mechanisms.

1.1. Heavy Metal Pollution of Soils

Soil has been recognized as the major sink for anthropogenic heavy metal deposition through various pathways. The contamination of soil by heavy metals can be problematic on several levels because they do not degrade biologically and this always result in several soil disfunctions leading to concerns about the environmental quality. Metal contaminated soil poses risks to humans and animals through ingestion of plants that have bioaccumulated toxic metals from contaminated soil [18]. Human activities all over the earth have increased environmental pollution by heavy metals in agricultural soil. Cadmium emissions have increased dramatically during the 20th century, one reason being that cadmium-containing products are rarely re-cycled, but often dumped together with household waste. At high concentrations, all heavy metals have strong toxic effects and are regarded as environmental pollutants. Excess concentrations of heavy metals in soils have caused the disruption of natural terrestrial ecosystems [19]. The components of soil may include exchangeable ions absorbed on the surfaces of inorganic solids, non exchangeable ions and insoluble inorganic metal compounds such as carbonates and phosphates, soluble metal compound or free metal ions in the soil solution, metal complex of organic materials, and metals attached to silicate minerals. Heavy metals affect the number, diversity and activities of soil microorganisms. The accumulation of heavy metals in agricultural soils has been a wide concern of the public, due to the food safety issues and potential health risks as well as its detrimental effects on soil ecosystems. Combined pollution with heavy metals has frequently been reported in many contaminated sites in China, such as in Wenzhou, Zhejiang Province. As a very toxic element, Cd is of primary concern in soil and food contamination, particularly in the rice cropping system. These potentially toxic elements accumulate in soils and induce a potential contamination of food chain and endanger the ecosystem safety and human health [20]. In Turkey, Cu, Cd and Zn-contaminated soils, which result from the improper disposal of ındustrial waste, are an environmental threat in many regions [13].

***Table 1**: Trace elements in soils and associated mineral concentration*

Elements	Normal range in soil(total) (μgg^{-1}dry weight)	Concentration in soil considered toxic (total) (μgg^{-1}dry weight)
Cr	5-1000	75-100
Mn	200-2000	1500-3000
Co	1-70	25-50
Ni	10-1000	100
Cu	2-100	60-125
Zn	10-300	70-400
Cd	0.01-7	3-8
Sn	<5	50
Hg	0.02-0.2	0.3-5
Pb	2-200	100-400

***Source:** [21].*

1.2. Sources of Heavy Metals Contamination of Soils

There are different sources of heavy metals in the environment such as (1) natural sources, (2) agricultural sources, (3) industrial sources, (4) domestic effluent, (5) atmospheric sources and (6) other sources. Heavy metal pollution can originate from both natural and anthropogenic sources. Activities such as mining and smelting operations and agriculture have contaminated extensive areas of world such as Japan, Indonesia and China mostly by heavy metals such as Cd, Cu and Zn and Cu, Cd and Pb in North Greece, in Albania and Cr, Pb, Cu, Ni, Zn and Cd in Australia [22]. Anthropogenic inputs are associated with industrialization and agricultural activities such as atmospheric deposition, waste disposal, waste incineration, urban effluent, vehicle exhausts, fertilizer application and long-term application of sewage sludge in agricultural land health [20]. Heavy metals of non-anthropogenic origin are always present at a background level with their occurrence in soils being related to weathering of parent rocks and pedogenesis. However, the concentration of several heavy metals has increased dramatically in certain ecosystems due to anthropogenic activities [23]. Some of the sources of heavy metals are the following.

Natural source: - Naturally heavy metals occur in soils, usually at a relatively low concentration, as a result of the weathering and other pedogenic processes acting on the rock fragments on which the rock develops soil parent materials The initial sources of heavy metals in soils are the parent materials from which the soils were derived, but the influence of parent materials on the total concentrations and forms of metals in soils is modified to varying degrees by pedogenetic processes. In areas affected lightly by human activities, heavy metals in the soils derived mainly from pedogenetic parent materials, and metals accumulation status was affected by several factors such as soil moisture and management patterns [24]. During weathering processes the primary crystalline structures of some rock minerals are completely broken and relevant chemical elements are thus either adsorbed in the topsoil or transported towards surface water or groundwater targets [25].

Mining:-. Mining is one of the most important sources of heavy metals in the environment. Mining and milling operations together with grinding, concentrating ores and disposal of tailings, along with mine and mill waste water, provide obvious sources of contamination. Therefore, large areas of agricultural land can be contaminated, including paddy field mines can become an important point source of toxic elements including As, Cd, Cu, Pb and Zn in the surface [26]. Heavy metals contained in residues coming from mining and metallurgical operations are often dispersed by wind, water (erosion) and by atmosphere within a distance and transported up to several kilometers away from their sources, transferred to the soil and accumulated in plants, animals and can then be passed up the food chain to human beings as a final consumer and cause adverse effect on the ecosystem around the metal mines [27], [28]. The pollution of soil and groundwater by dissolved heavy metals has mainly been associated with Acid Mine Drainage (AMD), one of the most serious environmental hazards of mining industry. The AMD is generated by the oxidation of sulfide bearing minerals exposed to weathering conditions, resulting in low quality effluents characterized by acidic pH, a high level of dissolved metals (e.g., As, Cd, Cu, Zn), and anions (e.g., sulphates and carbonates). Inappropriate treatment of tailings and acid mine drainage could pollute the agricultural fields surrounding the mining areas. Statistics show that over 10 million hectares of land in China are threatened by heavy metal contamination, with some 2 million hectares being mining areas. The Tongling copper mine in Anhui province in China, Long-term mining activities in this area had caused widespread metal pollution. The soil concentration of average total Cu was 618 mg kg-1, with a wide range of 78-2830 mg kg^{-1}. Lead concentration in soil also showed a large variability with a mean of 161 mg kg^{-1}. The total Zn concentration varied from 78 to 1280 mg kg^{-1}, with an average of 354 mg kg^{-1}. It was reported that the majority of the agricultural soils were contaminated with As. High As concentration in these soils may be attributed to arsenopyrite which is known to occur in many areas of Southeast Asia, especially in tin mining regions [29].

The study also conducted in Mormora River in Adola Goldfield of southern Ethiopia, including the Legadembi gold ore - many abandoned semi-mechanized hydraulic placer gold mining sites, abandoned and ongoing artisanal placer gold mining and exploration areas indicates the enrichment of elements above the Clarke of Concentration for Au, Pb, Zn, Cu, Ag, As, Sb, Mo and Ni [30]. Several trace elements including copper, lead, antimony, and arsenic are exclusively enriched in the ore zone and are positively correlated with gold and among each other. Heavy metal (lead, copper, nickel and cobalt) pollution of stream sediments was revealed in the area. The highest concentrations for Co, Ni, Cu, Zn and Pb were obtained from Stream, discharge, from the tailings dam and waste dump located south of the Legadembi open-pit. High concentrations of heavy metals (cobalt: 3.7mg/l, nickel: 2.4mg/l and copper: 1.1mg/l) were reported from water discharge of LGM tailings dam. These values are above the maximum permissible level of the 2001 Ethiopian Drinking Water Standards. This is confirmed by the presence of the highest value for zinc (178ppm) and the second highest value for copper (94ppm) obtained from the sediment sample taken at final discharge of the tailings dam. The few soil samples analyzed are found to be polluted with respect to cobalt, nickel, copper and zinc when the present results are compared with Dutch norms for soils. Deforestation, modification of landscape, disturbance of the fertile topsoil and turbidity of the waters are additional environmental impacts due to primary and placer gold mining in the area. [9].

Fertilizers and agrochemicals:- The inorganic and organic fertilizers (Fertilizer is a substance added to soil to improve plants growth and yield.) are the most important sources of heavy metals to agricultural soil include liming, sewage sludge, irrigation waters and pesticides, sources of heavy metals in the agricultural soils. Others, particularly fungicides, inorganic fertilizers and phosphate fertilizers have variable levels of Cd, Cr, Ni, Pb and Zn depending on their sources. Cadmium is of particular concern in plants since it accumulates in leaves at very high levels, which may be consumed by animals or human being. Cadmium enrichment also occurs due to the application of sewage sludge, manure and limes. Although the levels of heavy metals in agricultural soil are very small, but repeated use of phosphate fertilizer and the long persistence, time for metals, there may be dangerously high accumulation of some metals(. Several heavy metal–based pesticides (Pesticides kill unwanted pests) are used to control the diseases of grain and fruit crops and vegetables and are sources of heavy metal pollution to the soil [22]. Huge amounts of fertilizers are frequently applied to soils in concentrated farming systems to deliver suitable N, K and P for crop growth. The complexes used to offer these elements comprise rare quantity of heavy metals (for example Cadmium and Lead) as contaminations, that, after continual fertilizer application may meaningfully proliferate their quantity in the soil. Metals like Cadmium and Lead have no recognized physiological actions. Certain phosphatic fertilizer applications unintentionally add Cd and other possibly dangerous elements for the soil, including Fe, Pb and Hg. Heavy metals input to arable soils through fertilizers courses increasing concern for their potential risk to environmental health. It was reported that the phosphate fertilizers were generally the major source of trace metals among all inorganic fertilizers, and much attention had also been paid to the concentration of Cd in phosphate fertilizers. For instance, the great majority of agricultural soils in Malaysia are heavily fertilized by this kind of fertilizers. Soils in these southern Asian countries have P requirements, so that histories of P fertilizers addition, with associated with impurities (Cd, Cu, As, and Zn), seem to be greater on these countries. It was estimated that a total input of 5000 tons of Cu and 1200 tons of Zn were applied as agrochemical products to agricultural land in China annually [31].

Table: 2*. Guideline for safe limits of heavy metals Agricultural soil (µg g^{-1})*

Heavy metals	Cd	Cu	Pb	Zn	Mn	Ni	Cr
Indian standard	3–6	135–270	250–500	300–600	–	75–150	–
European union Standard	3	140	300	300	–	75	150

Source*: [22].*

Waste water irrigation:- Continued irrigation of agricultural soil can lead to accumulation of heavy metals such as Pb and Cd. The contamination of soil by heavy metals may also be from irrigation water sources such as deep wells, rivers, lakes or irrigation canals [22]. After long-term application of untreated wastewaters, significant amounts of heavy metals can accumulate in the soil at toxic levels. At present, heavy metals, such as Cr, Zn, Pb, Cd, Ni, etc., are commonly found in subsurface soil irrigated with wastewater. Once the adsorption site of the soil for heavy metals is saturated, more heavy metals would be distributed in the aqueous phase and the bioavailability of heavy metals would subsequently be enhanced [20].

2. Heavy Metals Toxicity and its Mechanisms

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Toxic heavy metals have the ability to replace vital minerals, for instance Cadmium, which is located just below zinc in the periodic table of the elements and has an atomic structure very similar to that of zinc almost fits perfectly in the zinc binding sites of critical enzymes such as RNA transferase, carboxypeptidase and alcohol dehydrogenase in the body [32]. Heavy metals can be poisonous for macro- and micro-organisms through direct influence on the biochemical and physiological procedures, reducing growth, deteriorating cell organelles, and preventing photosynthesis. In other word, humans and ecosystem may be exposed to chemical hazards such as heavy metals (lead, chromium, arsenic, zinc, cadmium, copper, mercury and nickel) through the direct ingestion of contaminated soils, consumption of crops and vegetables grown on the contaminated lands or drinking water that has percolated through such soils. Study indicates that subsistence farmers eating rice grain grown on contaminated sites throughout their lifetime are at risk from dietary exposure to cadmium [14]. Heavy metals produce their toxicity in organisms by forming complexes or "ligands" with organic compounds. These modified biological molecules lose their ability to function properly, and result in malfunction or death of the affected cells. Some heavy metals may form complexes with other materials in living organisms. These complexes may inactivate some important enzymes, systems and certain protein structures [33]. They "can bind to vital cellular components, such as structural proteins, enzymes, and nucleic acids, and interfere with their functioning [34].

2.1. Health Effects of Accumulation of Heavy Metals in Humans

Occurring as natural constituents of the earth‟s crust, heavy metals are by nature non-biodegradable and tend to be contaminants to living things in the environment. Although many heavy metals at low concentrations have an essential role as nutrients for plants, animals and human health, some if present at higher quantities and in certain forms may also be toxic and can cause harm to life . Therefore, the biota that inhabits contaminated sites is exposed to very high amounts of the heavy metals [35]. Following rapid social and economic development over the past several decades, soil pollution by heavy metals has been both serious and widespread. Heavy metal pollution is covert, persistent and irreversible. This kind of pollution not only degrades the quality of the atmosphere, water bodies, and food crops, but also threatens the health and well-being of animals and human beings by way of the food chain [36]. Generally, Absorption of heavy metals in low doses by humans over a long period of time through food has been shown to have resulted in serious health consequences [37]. Heavy metal uptake by crops growing in contaminated soil is a potential hazard to human health because of transmission in the food chain. Metal-mediated formation of free radicals causes various modifications to DNA bases, enhanced lipid peroxidation, and alters calcium and sulphydryl homeostasis. Moreover, lipid peroxides, formed by the attack of radicals on polyunsaturated fatty acid residues of phospholipids, can further react with redox metals finally producing mutagenic and carcinogenic malondialdehyde, 4-hydroxynonenal and other exocyclic DNA adducts (etheno and /or propane adducts). The redox active ones such as iron, copper, chromium, vanadium and cobalt possess the ability to produce reactive radicals such as superoxide anion radical and nitric oxide in biological systems, whereas the redox inactive ones such as arsenic, cadmium, lead, mercury, nickel show their toxic effects via bonding to sulphydryl groups of proteins and depletion of glutathione. Despite many years of research we are still far away from effective treatment against toxicity caused due to exposure to heavy metals/metalloids[19].

***Table: 3** Toxic Effects of different Heavy Metals and Its limitation in (ppm)*

Heavy Metals	EPA	WHO	Toxic Effects
Ag	0.10		Cause skin and other body tissues to turn gray or blue-gray, breathing problems, lung and throat irritation and stomach pain.
Cd	5.0	0.05	Carcinogenic, mutagenic, endocrine disruptor, lung damage, hypertension, skin cancer, and peripheral vascular disease, bone defects (osteomalacia, osteoporosis) in humans and animals and fragile bones, affects calcium regulation in biological systems
Cu	1.3	2	Brain and kidney damage, elevated levels result in liver cirrhosis and chronic anemia, stomach and intestine irritation include anorexia, fatigue, premenstrual syndrome depression, anxiety, migraine headaches, allergies, childhood hyperactivity and learning disorders
Hg	2.0		Autoimmune diseases, depression, drowsiness, fatigue, hair loss, insomnia, loss of memory, restlessness, disturbance of vision, tremors, temper outbursts, brain damage, lung and kidney failure
Ni		0.2	Allergic skin diseases such as itching, cancer of the lungs, nose, sinuses, throat through continuous inhalation, immunotoxic, neurotoxic, genotoxic, affects fertility, hair loss with hyperglycemia, depression, sinus congestion, fatigue, reproductive failures and growth problems in humans
Pb	15	0.01	Excess exposure in children causes impaired development, reduced intelligence, short-term memory loss, disabilities in learning and coordination problems, risk of cardiovascular disease Disruption of the biosynthesis of haemoglobin and anaemia, a rise in blood pressure, effects on the kidneys, gastrointestinal tract, skeletal, circulatory, enzymatic, endocrine, and immune systems joints and reproductive system and acute or chronic damage to the nervous system
Zn	0.5		cause impairment of growth and reproduction
Cr		0.02	skin rashes, stomach upset and ulcer, respiratory problems, weakened immunesystems, kidney and liver damage, alteration of genetic material, cancer and death

Source: [15] - [23] - [35].

3. Bioavailability and Bioaccumulation of Heavy Metals in Plants

Bioavailability is the proportions of total metals that are available for incorporation into biota (bioaccumulation). Total metal concentrations do not necessarily correspond with metal bioavailability. In soil, metals exist as a variety of chemical species in a dynamic equilibrium governed by soil physical, chemical, and biological properties. In general, only a fraction of soil metal is readily available (bioavailable) for plant uptake. The bulk of soil metal is commonly found as insoluble compounds and unavailable transport into roots. In soil, some metals, such as Zn and Cd, occur primarily as soluble or exchangeable, readily bioavailable form. Others, such as, Pb occur as insoluble precipitates (phosphates, carbonates, and hydroxy-oxides) which are largely unavailable for plant uptake [38]. Plants cannot usually access the total pool of a metal present in the growth substrate. Instead, that fraction of the metal which plants can absorb is known as the available or bioavailable fraction. The risks for both environment and human health from toxic heavy metals (specifically Cd, Cr, Cu, Ni, Pb, and Zn) are associated with the forms bioavailable to plants. Bioavailability and phytoavailability are terms used to describe the degree to which contaminants are available for absorption or uptake by living organisms that are exposed to them. Plants respond only to the fraction that is "phytoavailable" to them. For heavy metal phytoremediation (phytoextraction in particular), bioavailability of metals in contaminated soils, is a crucial factor regulating heavy metal uptake by plant roots. However, metal phytoavailability is a complex phenomenon that is dependent on a cascade of related factors [39]. Lead is a major metal contaminant notorious for posing a significant risk to humans, especially children. For example, it has been estimated that in the USA alone lead poisoning affects more than 800 000 children between the age of one and five. The potential for Pb phytoextraction is limited primarily due to low soil mobility and little propensity for lead uptake into roots [38].

3.1. Factors Affecting Heavy Metals Mobility and Phytoavailability in Plants

Metals present in a soil can be divided into a number of fractions including; the soluble metal in the soil solution, metal-precipitates, metal sorbed to clays, hydrous oxides and organic matter, and metals within the matrix of soil minerals. These different fractions are all in dynamic equilibrium with each other. However, while the soluble metal in the soil solution is directly available for plant uptake other soil metal pools are less available. For example, change in the concentration of metal in the matrix of soil minerals is slow relative to exchange and desorption reactions between clays, hydrous oxides, organic matter and the soil solution. Metals within the soil solution are the only soil fraction directly available for plant uptake. Hence, factors which affect the concentration and speciation of metals in the soil solution will affect the bioavailability of metals to plants. Soil factors which have an effect on metal bioavailability include the following [40], [41].

Soil pH: Soil pH is a major factor influencing the availability of elements in the soil for plant uptake. Under acidic conditions, H^+ ions displace metal cations from the cation exchange complex of soil components and cause metals to be released from variable-charged clays to which they have been chemisorbed i.e. specific adsorption. The retention of metals to soil organic matter is also weaker at low pH, resulting in more available metal in the soil solution for root absorption. Many metal cations are more soluble and available in the soil solution at low pH (below 5.5) including Cd, Cu, Hg, Ni, Pb, and Zn. It is suggested that the phytoextraction process is enhanced when metal availability to plant roots is facilitated through the addition of acidifying agents to the soil [42]. Increases in soil pH decreased with availability of Cd and Zn to the plant roots [41]. Soil pH directly influences the phytoavailability of metals as soil acidity determines the metal solubility and its ability to move in the soil solution. Metal cations are the most mobile under acidic conditions while anions metals are released into the soil solution due to competition with H^+ ions. At high pH, cations precipitate or adsorb to mineral surfaces and metal anions are mobilized. At neutral or alkaline pH, most of the metals in soil are not available to plants, especially Pb and Cr are inherently immobile. For enstance, in the Enyigba-Abakaliki mine transect, the mean soil pH was 6.01; soil had the highest contents of Zn and Cd [43]. Decreasing pH in soils increases the competition between H^+ and dissolved metals for ligands such as CO_3^{2-}, SO_4^{2-}, Cl-, OH-, S^{2-} and phosphates. This increased competition decreases the metal adsorption capacity of soil particles, leading to increased mobility of heavy metals, which ultimately boosts the bioavailability of the metals in the soil [44].

Soil Organic Matter: Metal ions can be complexed by organic matter altering their availability to plants. The COO groups in both solid and dissolved organic matter form stable complexes with metals. Hence, as the amount of organic matter present in soil increases the opportunity for forming stable metal-organic matter complexes increases. In general, plants are unable to absorb the large metal-complexes and so the bioavailability of metals decreases [40]. The organic matter is one of the factors that may reduce the ability of metals to be phytotoxic in the soil due to metal-organic complexation. The presence of organic carbon increases the cation exchange capacity of the soil which retains nutrients assimilated by plants. Increasing the amount of organic matter in the soil helps to minimize the absorption of heavy metals by plants. Land rich in organic matter actively retains metallic elements. Soils with relatively low organic matter concentration are more susceptible to contamination by trace elements. Compost amendments to contaminated soils containing labile elements reduce the overall bioavailabilities of metals due to sorption processes [39**].**

Redox Potential- The oxidation/reduction (redox) conditions of a soil can play a role in the availability of metals. The redox status of the soil can be affected by many factors including water logging and compaction. Redox conditions can affect the availability of metals by affecting the proportion of particular metal species (e.g. Mn(II) vs. Mn(IV) in the soil solution and by affecting the solubility of metals in the soil solution. [40]. Redox potential in soil is established by oxidation-reduction reactions resulting from microbial activity. These redox reactions convert contaminants into non-hazardous or less toxic compounds that are more stable, less mobile and/or inert. However, in soil environments, these reactions tend to be relatively slow. Lack of oxygen in the soil causes start-up and increase the mobility of the large part of heavy metals. Manganese can exist in soil as Mn(II), Mn(III) and Mn(IV), however only the reduced Mn(II) form is stable in solution.Manganese (II) is the most soluble form of Mn and so under reducing conditions higher concentrations of Mn^{2+} will be present in the soil solution. Conversely, under more oxidising conditions, soil solution concentrations of Mn decrease because the equilibrium shifts in favour of Mn(III) and Mn(IV) which tend to exist mainly as insoluble hydroxides and oxides. For example, increasingly reduced conditions corresponded with an increase in the highly bioavailable Mn^{2+} in the soil solution and a corresponding increase in Mn uptake by Oryza sativa (rice) plants. Under waterlogged conditions increases in Mn uptake and symptoms of Mn toxicity have been noted in Malus sp. (apple) and Pyrus sp. (pear) trees. Hence, reducing soil conditions, such as flooding and soil compaction, tend to increase the availability of soil Mn and enhance toxicity Most Cu and Zn are present as the divalent form in soils with the monovalent forms being highly unstable. Hence, neither Cu nor Zn tend to be significantly reduced under low redox conditions [39].

4. Phytoremediation of Heavy Metals Polluted Soils

Phytoremediation is a word formed from the Greek prefix “phyto” meaning plant, and the Latin suffix “remedium” meaning to clean or restore. Plants act as solar-driven pumping and filtering systems as they take up contaminants (mainly water soluble) through their roots and transport/translocate them through various plant tissues where they can be metabolized, sequestered, or volatilized [14]. Immobilisation or extraction by chemicals is expensive, requires a technically complex process and is often appropriate only for small areas where rapid, complete decontamination is required. This process generally has adverse effects on biological activity, soil structure and fertility. The requirements of these methods make them unaffordable for poor countries. Recent developments in the field of environmental restoration have led to invention of the phytoremediation technique. It is a low cost, long term, environmentally compatible solution for remediating some of heavy metal contaminated sites and aesthetically friendly method of immobilizing/stabilizing, degrading, transferring, removing, or detoxifying contaminants, including metals, pesticides, hydrocarbons, and chlorinated solvents. Over the past 2 decades, it has become a highly accepted means of detoxifying contaminated water and soil (U.S.EPA, 2001) [12]. Specifically, several subsets of metal phytoremediation have been developed and they include: (1) phytostablization, in which plants stabilize the pollutants in soils, thus rendering them harmless; (2) phytoextraction, in which heavy metal hyperaccumulators, high-biomass, metal-accumulating plants and appropriate soil amendments are used to transport and concentrate metals from the soil into the above–ground shoots, which are harvested with conventional agricultural methods; (3) phytofiltration or rhizofiltration, in which plant roots grown in aerated water, precipitate and concentrate toxic metals from polluted effluents; and phytovolatilization, in which plants extract volatile metals (e.g., Hg and Se) from soil and volatilize them from the foliage **[45].**

Table:* *4 Mechanism and Selection criteria of plant species.

Mechanism	Definition and description	Selection criteria of plant species
Phytoextraction	Uptake of a contaminant from soil by plant roots and its translocation into harvestable plant where they accumulate.	Tolerance to high concentrations metals; - High metal accumulation capability; - Rapid growth rate; -Easy to harvest; - Accumulation of trace elements in the above ground parts; - Extended root system for exploring large soil volumes; - High translocation factor; - Easy agricultural management; - Good adaptation to prevailing environmental and climatic conditions; - Resistance to pathogens and pests;
Phytostabilization	In phytostabilization, plants are responsible for reducing the percolation of water within the soil matrix, which may create a hazardous leach ate, inhibiting direct contact with polluted soil by acting as barrier and interfering with soil erosion,which results in the spread of toxic metals to the other sites	The ability to develop extended and abundant root systems; - The ability to keep the translocation of metals from roots to shoots as low as possible; - The capacity to retain the contaminants in the roots or rhizosphere (excluder mechanism) to limit the spreading through the food chain.
Phytovolatilization	extract volatile contaminants, such as Hg and Se, from polluted soils and to ascend them into the air from their foliage. In other word, it involves the use of plants to take up contaminants from the soil, transforming them into volatile forms and transpiring them into the Atmosphere	
Rhizofiltration	It is primarily used to remediate extracted groundwater, surface water and wastewater with low contaminant concentrations. The use of plant roots to absorb or adsorb contaminants that are in solution surrounding the root zone	Metal-resistant plants; - High adsorption surface; - Tolerance of Hypoxia; - Terrestrial plants are preferred because they have a fibrous and much longer root system, increasing the amount of root area.

Sources:[39]-[41]-[46].

4.1. Mechanisms of Phytoremediation

In their natural environment plants survival, growth and reproduction depend on the soil physical and chemical characteristics changes. To survive such changes, plants must adapt and those that fail to be eliminated [17]. Physiological mechanisms have been evolved by plants which colonized metalliferous or highly mineralized soils enabling them have tolerance of metal toxicity. Generally, these mechanisms do not suppress metal uptake but the resultant impact is internal detoxification. Plants may be classified as accumulators or indicators or excluders with respect to any particular element. Accumulators can take up high concentrations of certain heavy metals without the plants having any toxicity effect and as related to hyperaccumulators which concentrate inordinate amounts of trace elements in the aerial portions or shoots in their above background biomass. The basis of hyperaccumulation is "elemental defence" for plants to excessively concentrate heavy metals as a defence mechanism against natural enemies, such as herbivores [43]. Plants have a range of potential mechanisms at the cellular level that might be involved in the detoxification and tolerance to heavy metal stress. These all appear to be involved primarily in avoiding the build-up of toxic concentrations at sensitive sites within the cell, thus preventing the damaging effects. When metals accumulate in tissues they often cause toxicity, both directly by damaging cell structure and indirectly via replacement of other essential nutrients. The strategies for avoiding heavy metal build-up are diverse. Metal build-up can be the stimulation of the efflux of metals into the apoplast. As an example, stimulation occurred, and that the apoplastic accumulation of Pb was very significant in Azolla filiculoides-, or the chelation in cytosol by various ligands. Ligands such as phytochelatins and metalotheins promote the detoxification abilities of metals in the plant, as shown for the engineered Nicotiana tabacum. Some species, including Jatropha curcas (from Euphorbiaceae), Dodonaea viscose (from Sapindaceae) and Cassia auriculata (from Fabaceae), had potential for remediation of soils polluted with different kinds of trace and major elements. Also, high heavy metal accumulating ability has been reported for cereal crops such as maize (Zea mays L.), sorghum (Sorghum bicolor) and alfalfa (Medicago sativa L.) [14]. Crops like alpine pennycress (Thlaspi caerulescens), Ipomea alpine, Haumaniastrum robertii, Astragalus racemosus, Sebertia acuminate have very high bioaccumulation potential for Cd/Zn, Cu, Co, Se and Ni, respectively. Maize (Zea mays L.), Indian mustard (Brassica juncea L.), and sunflower (Helianthus annuus L.) have reportedly shown high uptake and tolerance to heavy metals. Among the plants of the Brassica species, the Brassica juneca deserve special attention because its relevance to the process of phytoexctration of heavy metals from soil was confirmed in many experiments. It has been found that B. juncea exhibits a high capacity to accumulate Cd- mainly in the shoots, where Cd level was recorded at level of 1450 µg Cd/g dry wt. This is three times more than reported in Brassica napus (555 µ g/g dry wt). In addition, this plant exhibit a high removal efficiency of other metals such as Pb (28% reduction) and this plant is more effective at removing Zn from soil. This is due to the fact, that B. juneca produces ten-times more biomass than T. cearullescens. Some species, such as cabbage (Brassica oleracea L.), lettuce (Latuca sativa L.) and tobacco (Nicotiana tabacum L.), accumulate high levels of Cd in leaves rather than in roots and increases or decreases the bioavailability of metal ions. [14].

Plant response Mechanisms to heavy metals

Uptake and accumulation of heavy metals by plants involve a series of mechanisms such as the use of specific genes as transporter, efflux pumps and chelating agents. Metallophyte species exhibit tolerance mechanisms to toxic heavy metals by using chemically suitable ligands to form stable non-toxic complexes which are then taken up and sequestrated into vacuoles. Some plant species express tolerance by compartmentalization and detoxification of the toxic metals in their root cells by complexation with amino acids, organic acids or metal-binding peptides[44]. Alternatively, plant species may use excluding mechanisms by hindering uptake of heavy metals into root cells through entrapment in the apoplastic environment or by binding to anionic groups of cell walls [47]. For instance, barley plants exposed to Al exuded high amounts of malic, citric and succinic acids and these enhanced tolerance in the plant compared to Al-sensitive plants. Plants have three basic strategies for growth on metal contaminated soil; Metal excluders, Metal indicators, hyperaccumulator.

Metal excluders:- Metal excluders are plants which effectively limit the levels of heavy metal translocation within them and maintain relatively low levels in their shoot over a wide range of soil levels; however, they can still contain large amounts of metals in their roots. They prevent metal from entering their aerial parts or maintain low and constant metal concentration over a broad range of metal concentration in soil; they mainly restrict metal in their roots. The plant may alter its membrane permeability, change metal binding capacity of cell walls or exude more chelating substances.

Metal indicators: - Species which actively accumulate metal in their aerial tissues and generally reflect metal level in the soil. They tolerate the existing concentration level of metals by producing intracellular metal binding compounds (chelators), or alter metal compartmentalisation pattern by storing metals in non-sensitive part [41]-[48]

Hyperaccumulators: - Metal accumulators hyper-accumulators are plant species tolerate, uptake, and translocate high concentrations of certain heavy metals in their above-ground tissues to levels far exceeding those present in the soil. These plants are capable of extracting heavy metals from soils and concentrate them in their shoots, to levels far exceeding than soil and they are widely used in phytoremediation [17]. To classify a given plant as a hyperaccumulator, the concentration criterion depends on the type of metal. For example, a Cd uptaken by a plant becomes toxic when its concentration in plant tissues is >100 mg/kg of dry matter for Cd, or when >1000 mg/kg for Ni, Cr, Pb, Co, As and Cu dry weight (DW) in leaves, or when >10,000 mg/kg dry weight of shoots for Zn and Mn, in case they are grown in metal-rich soils [47]-[49].

***Table:* 5** *Plant species and Metal Maximum concentration (mg kg^{-1}) as hyper accumulator species of different metals.*

Metals	Plant Species	Concentration of metal accumulated (mg/kg)
Ni	Thalaspi spp. (Brassicaceae)	200 - 31,000
	Alyssium spp (do)	1280 – 29,400
	Berkheya codil (Asteraceae)	11,600
	Pentacacalia spp (do)	16,600
	Psychotria corinota (Rubiaceae)	25,540
	Psycotria vanhermanni	35720
	Psycotria glomerata	10250
	Garcinia bakeriana	7440
	Streptanthus polygaloydes	14800
	Maytenus bureaviana	33750
Zn	Thalaspi caerulescene (Brassicaceae)	43,710
	Thalaspi rotundifolium (do)	18,500
Pb	Minuartia verna (caryophyllaeceae)	20,000
	Agrostis tenius (Poaeceae)	13,490
	Vetiveria zizaniodes	>1,500
	Armeria maritime	1600
Co	Crotolaria Cobalticola (Fabaceae)	30,100
	Haumaniastum robertii (Lamiuceae)	10,232
Cu	Ipomea alpine (convolvulaceae)	12,300
	Aeollanthus subacaulis	13700

Sources: *[46]-[50].*

4.2. Advantages and Limitations of Phytoremediation Mechanisms

Advantages	**Limitations**
Low capital and operating cost; - Metal recycling provides further economic advantages	Slower compared to other techniques and seasonally dependent; -Most of the hyperaccumulators are slow growers.
Permanent treatment solution; - Capable of remediating bioavailable fraction of contaminants; - Capable of mineralizing organics; - The potential to treat sites polluted with more than one type of pollutant; - It is restricted to the rooting depth of remediative plants; - Highly-specialized personnel not required; - Can be used for site investigation or after closure	Not capable of 100% reduction; - High contaminant concentration may be toxic to plants; - Soil phytoremediation is applicable only to surface soils; - Restricted to sites with low contaminant concentrations; - Requires technical strategy, expert project designers with field experience that choose the proper species and cultivars for particular metals and regions.
In situ application avoids excavation and transport of polluted media; - Relatively easy to implement	The presence of multiple types of heavy metals and organic contaminants may pose a challenge; - Climatic conditions are a limiting factor.
Reduce the risk of spreading the contamination; - Eliminate secondary air or water borne Wastes; - Public acceptance due to aesthetic reasons.	Metals can be washed by rain and transported back into the soil du the decomposition of plant biomass; - The use of invasive, non-native species can affect biodiversity; - Risk of food chain contamination in case of mismanagement and lack of proper care.

Sources: *[12]-[14]-[39]-[41].*

5. Criteria for Heavy Metals Accumulation in Plants

The ability of a plant species to clean up a metal-contaminated site depends upon the amount of metals that can be accumulated by the candidate plant, the growth rate of the plant and the planting density. There are several factors which decide the ideal plant for phytoremediation [51]. Generally, the ideal plants for phytoextraction should have high capacity to accumulate toxic levels of metals in their aerial parts (shoots), high growth rates, and tolerance to high salinity and high pH. Moreover, these plants must produce high dry biomass, easily grown and completely harvestable, and High levels of plant uptake and translocate metals, accumulate in harvestable tissues of the plant (to aerial parts efficiently). Overall, it is recommended to use the native plant species that grow locally near the site [12]. The main criteria for hyper-accumulators are;

Accumulating capability:- Accumulating capability is the natural capacity of plants to accumulate metals in their above-ground parts (the threshold concentration) in amounts greater than 100 mg kg-1 for Cd, 1000 mg kg-1 for Cu, Cr, Pb, and Co, 10 mg kg-1 for Hg and 10000 mg kg-1 dry weight of shoots for Ni and Zn.

Tolerance capability:- Tolerance capability is the ability of plants to grow in heavy metal-contaminated sites and to have considerable tolerance to heavy metals without showing any reverse effects, such as chlorosis, necrosis, whitish-brown color, or reduction in the above-ground biomass (or at least not a significant reduction)

Bioconcentration factor (BCF)**: -** Phytoextraction potential can be estimated by calculation of bioconcentration factor (or biological absorption coefficient) and translocation factor. The bioconcentration factor (BCF), which is defined as the ratio of the total concentration of element in the harvested plant tissue (C plant) to its concentration in the soil in which the plant was growing (C soil) [52].

$$BCF = \frac{Cplant}{Csoil}$$

Translocation factor (TF):- TF is the capability of plants to take up heavy metals in their roots and to translocate them from the roots to their above-ground parts (shoots). TF, defined as the ratio of the total concentration of elements in the aerial parts of the plant (C, shoot) to the concentration in the root (C, root), is calculated as follows

$$TF = \frac{Cshoot}{Croot}$$

It is reported that excluders can be identified by a TF < 1, whereas accumulators are characterized by a TF > 1 and BCFs and **TF**s are > 1 in hyper accumulators **[44].**

Future Prospects

Rapid industrialization and technology development have adverse side effects like soil contamination and degrading soil health. Research related to this relatively new technology needs to be promoted and emphasized and expanded in developing countries since it is low cost, does not have the destructive impact on soil fertility and structure that some more vigorous conventional technologies have such as acid extraction and soil washing.

6. Conclusion

The rapid industrialization and intensive agricultural activities over the last few decades have resulted in accumulation of various pollutants in the environment, especially heavy metals. Heavy metals are one of the most critical threats to the soil and water resources, as well as to human health. Contamination with heavy metals can affect the whole environment, but a major environmental concern and the longest-lasting effects due human activities is the contamination of soils. These metals are released into the environment through mining, smelting of metal ores, industrial emissions, and the application of pesticides, herbicides and fertilizers. Metals, such as Cd, Cu, Pb, Zn, and metalloids (e.g. As), are considered to be environmental metallic pollutants, due to their persistence, bioaccumulative nature and causing the serious health problem to human and other animals. Therefore decontamination of heavy metal-contaminated soils is very important for maintenance of environmental health and ecological restoration. The high cost of existing cleanup technologies led to the search for new cleanup strategies that have the potential to be low-cost, low-impact, visually benign, and environmentally sound. Phytoremediation is a new cleanup concept that involves the use of plants to clean or stabilize contaminated environments. Phytoremediation of metals is the most effective plant-based method to remove pollutants from contaminated areas. This green technology can be applied to remediate the polluted soils without creating any destructive effect of soil structure. Some specific plants, such as herbs and woody species, have been proven to have noticeable potential to absorb toxic metals. These plants are known as hyperaccumulators. Thus, Phytoremediation is becoming an important tool for decontaminating soil, water, and air by detoxifying, extracting, hyperaccumulating, and/or Sequestering contaminants, especially at low levels where, using conventional methods, costs exceed effectiveness.

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