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BIOTRANSFORMATION AND REMOVAL OF HEAVY METALS: A REVIEW OF PHYTOREMEDIATION AND MICROBIAL REMEDIATION ASSESSMENT ON CONTAMINATED SOIL

C.U. Emenike 1,2,3*, B. Jayanthi 1, P. Agamuthu 1,2, S.H. Fauziah 1,2
1Institute of Biological Sciences, University of Malaya, 50603 Kuala Lumpur, Malaysia
2Centre for Research in Waste Management, Institute of Research Management & Monitoring, University of Malaya, 50603 Kuala Lumpur, Malaysia
3Faculty of Science, Hezekiah University, Umudi, Imo State, Nigeria

*Corresponding author: Emenike C.U
Email: emenike@um.edu.my/emenikecu@gmail.com

ABSTRACT
Environmental deterioration is caused by a variety of pollutants; however, heavy metals are often a major issue. Development and globalization has now also resulted in such pollution occurring in developing societies, including Africa and Asia. This review explores the geographical outlook of soil pollution with heavy metals. Various approaches used to remedy metal-polluted soils include physical, chemical, and biological systems, but many of these methods are not economically viable, and they do not ensure restoration without residual effects. This review evaluates the diverse use of plants and microbes in biotransformation and removal of heavy metals from contaminated soil. Mechanisms on how natural processes utilizing plants (phytoremediation) and microorganisms (bioremediation) remove or reduce heavy metals from soil at various levels are presented. This review concludes that remediation technologies are necessary for the recovery of metal-contaminated environments and the prevention of continuous environmentally toxic impacts on living organisms.

Keywords: Bioremediation, Heavy Metals, Phytoremediation, Pollution, Soil

1.0 INTRODUCTION
Environmental protection is an important factor in ensuring a functional and balanced ecosystem. A number of environmental pollutants cause high-level degradation impacts on ecosystem
components, especially soil. Metals exist within the environment and inevitably appear at varying concentrations. An excess in the required concentration results in heavy metal pollution or contamination.

Heavy metal chemically refers to a class of a distinct subdivision of elements characterized with metallic properties. Transition metals, certain lanthanides, metalloids, and actinides, comprise heavy metals. The various properties of heavy metal include a density range of 3.5–7 g/cm$^3$, atomic weight ranging from 22.98 to < 40, and atomic number of <2 (Afal and Wiener 2014). Similarly, substances at a pure state possess high and useful electrical and thermal conductivities. Five different fractions of metals are present in soil due to differences in their properties, namely soil solution dissolution, binding potential properties for the location exchange of inorganic soil constituent, adsorption to inorganic soil constituents, attachment to insoluble organic matter, and precipitation potential from pure or mixed solids (Ann 2005). A total of 92 elements exist in nature, and about 30 of these are metalloids. The elements Be, B, Li, Al, Ti, V, Cr, Mn, Co, Ni, Cu, As, Se, Sr, Mo, Ag, Cd, Sn, Sb, Te, Cs, Ba, W, Pt, Au, Hg, Pb, and Bi may be especially harmful to humans (Mingho 2005).

The availability or entry of heavy metals into the ecosystem originates from diverse sources that are either natural or anthropogenic. Significant sources include geological weathering, mineral exploration, soil erosion, industrial discharge, agricultural use of chemicals for pest or disease control, and other factors (Mingho 2005). Some metals, such as Hg and As, are still used in gold mining and wood preservation. Tetraethyl remains the most commonly used petrol additive. Nonetheless, the trend is significantly low in developed countries. Living organisms require some types of heavy metals at certain amounts, but excessive levels are considerably carcinogenic or toxic (Dewan 2009). The elements with the highest toxicity are typically arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cu), copper (Cr), manganese (Mn), and nickel (Ni) (Poovey 2001). Humans require Co, Cu, Cr, Mn, and Ni in small amounts. Nonetheless, other heavy metals are carcinogenic or toxic, and they can cause severe effects or illness. Some metals interact with the biomolecules of the human body to generate biotoxic compounds that are remarkably stable with a low dissociating ability (Duruibe et al. 2007). Mn, Hg, Pb, and As can interfere with the central nervous system. Similarly, Hg, Pb, Cd, and Cu cause problems to the excretory organs, especially kidneys, whereas bone or teeth formation is susceptible to the effects of Ni, Cd, Cu, and Cr (Kumar 2013). Humans are commonly exposed
toxic heavy metals through water consumption, through the food chain, or through high ambient air concentrations near emission sources (Lenntech 2004). For example, the Love Canal tragedy in the City of Niagara, USA, shows the detrimental impact of metal contamination of soil and groundwater on the human population (Fletcher 2002). According to the Agency for Toxic Substance and Disease Registry (ATSDR), heavy metals above the concentration limit can pose a threat to human health and cause chronic adverse effects (ATSDR, 2003a, 2003b, 2007, 2008; Castro and Mendez 2008). The entry of soil-borne heavy metals into the food chain depends on the amount and source of metal input, the soil properties, the rate and magnitude of uptake by plants, and the extent of absorption by animals (Adriano 2001). The total concentration alone cannot determine the mobility and toxic effects of metals on the soil. Chemical specificities, such as metallic properties, bond states, and environmental conditions, are collective determinants. Similarly, soil properties, especially pH levels, organic matter compositions, redox conditions, and the presence of chelating exudates, often influence metal toxicity and mobility in soil (Nyamangara 1998). Many tragic cases occur in humans due to consumption of fish products that contain methyl mercuric compounds, which tend to form when aquatic organisms biomethylate mercuric salts. Such poisoning, which occurred in Minamata Bay in Japan, was eventually referred to as the Minamata disease of 1950 (Knopf and Konig 2010). Recent cases of human health risks due to As poisoning were recorded in Bangladesh, India, and China, where millions of people are at risk (Bhattacharya 2012). Previous Cd accumulation in the offal of grazing animals in New Zealand and Australia also made them unsuitable for human consumption, thereby affecting access to meat products for overseas markets (Loganathan et al. 2008).

2.0 IMPACTS OF HEAVY METALS

2.1 Impacts on the soil

Soil is the major sink of heavy metals due to its various anthropogenic activities. Heavy metals alter the composition and activity of soil microbial communities (Yan et al. 2016). High concentration of heavy metals in the soil results in high soil toxicity (Chao et al. 2014). The enzyme activity in heavy metal-contaminated soil is reduced significantly (10–50 times) compared with that in noncontaminated soil (Chander et al. 1995). Examples of common heavy
metals include Pb, As, Cr, Ni, Zn, Cd, Cu, and Hg (Wuana and Okieman 2014). Heavy metals may persist in soil for a considerably long time (Adriano 2003).

Marques et al. (2009) indicated that heavy metals include exchangeable ions that are absorbed by inorganic solids on the surface. Insoluble inorganic and nonexchangeable ion compounds, such as carbonates and phosphates, are compounds from soluble metals (free metal ions), organic metal complexes, and metals attached to silicate minerals. Metals that exist naturally in the soil cause no contamination, unlike the metals that occur due to anthropogenic activities with separate entities or those present in high concentrations (Ramos et al. 1994). The presence of heavy metals in soil also affects the soil pH (Harter 1983), organic matter, density and type of charge in soil colloids, degree of complexation with ligand and soil, soil relative surface area (Norvell 1984), and soil soluble concentrations (Marquoes et al. 2009). Metals induce toxic effects on soil microbes, and the degree of impact varies due to physiochemical conditions, such as pH, temperature, clay minerals, abundance of organic matters, inorganic anions and cations, and chemical forms of the metal (Baath 1989). They also reduce organic matter decomposition in the soil and nutrient recycling (Chao et al. 2014).

2.2 Impacts on plants

Heavy metal accumulation above the tolerance level in plants also induces adverse effects on the plant. The plant becomes remarkably toxic, and it may ultimately die. Hence, some plants tolerate metal toxicity until the threshold level. Two aspects of plant heavy metal interaction are as follows: (i) metal-induced impairment of plant development and (ii) resistive adaptation of plants to metal toxicity through modified metabolism (Cheng 2003). Heavy metals can interfere with the biological and physiological processes that are crucial to plant growth (Chibuike and Obiora 2014). A contaminated plant may exhibit reduced yield production, which consequently affects the food chain. Cytoplasmic enzyme inhibition and cell structure damage due to oxidative stress occur when the plant is contaminated with a heavy metal (Assche and Clijsters 1990; Jadia and Fluker 2009). An example of an indirect toxic effect is the replacement of essential nutrients at the cation exchange sites of plants (Taiz and Zeiger 2002). For example, Zaier et al. (2010) reported that the water content of Brassica juncea plants remarkably decreases under Pb toxicity, although this species is considered tolerant. Servilia et al. (2005) demonstrated that plants exposed to heavy metal exhibit stunted growth, deformation, reduced physicochemical activities, and overall alteration of cellular metabolism. Their measurements also revealed that
Heavy metals affect the growth and photosynthetic pigments of the plants. Table 1 shows the specific effects of metals on plants. Hg, As, Pb, Cd, and Cr are ranked among the most toxic metals that display considerable public health significance (Tchounwou et al. 2012).

### 2.3 Impacts on human health

Heavy metal contamination in the environment can directly affect humans through dust inhalation or skin absorption. Table 2 presents the toxic effects of excess concentrations of heavy metals on human health. According to McLaughin et al. (2000) and Ling et al. (2007), heavy metal contamination in soil poses a threat to both humans and ecosystems through direct ingestion or contact with contaminated soil. In the food chain, toxicity occurs in the following order: soil > plant > human or soil > plant > animal > human. Heavy metal contamination in soil also affects human health through drinking of contaminated groundwater and consumption of contaminated plants; this contamination also induces reduced agricultural production (Wuana and Okieimen 2011). A case study reported by Yabe et al. (2010) showed that about 30% of Chinese children possess blood containing Pb levels in excess of the 100 g/L limit. Heavy metal exposure occurs through water, fish, soil, food crops, food animals, and toys. This exposure results in metal toxicity in children, which can cause damage to organs and body systems. Cd emissions have increased remarkably in recent years, especially with its presence in household waste. Excess Cd exposure levels are also reported in Europe (Lars 2013). Another example of metal toxicity affecting human health is evident in a study conducted at the cement facility in Sagamu, Nigeria. Findings revealed significant noncancerous risks to children and adults who are 6–30 years old due to oral exposure to Cd and Cr from the facility. The levels are more than the allowable limits of noncancer hazard quotient. The cumulative hazard quotient index (THI) is significantly high to cause health hazards, especially due to the Cd contribution (Oluseye et al. 2013). Moreover, in Heshan Village, China, farmers were affected by As due to a As processing factory located in the village between 1951 and 1978. Since this period, the surrounding environment has been highly polluted with high As levels. Soil and water are highly contaminated with As above the prescribed level, and workers suffer from severe As poisoning. The surrounding plant and crops die or become too toxic for consumption. According to the Phoenix Satellite TV (2014), a total of 400 workers died due to As-induced cancer from 1951 to 2014. Cancer can be skin, liver, lung, colorectal, or uterine cancer.
3.0 ENVIRONMENTAL MEDIA AND HEAVY METAL DISTRIBUTIONS

Heavy metals in water, soil, air, and other environmental media present considerable environmental concern because of their potential long-term effects on human health, particularly in developing countries where remedial techniques are nascent (Emenike et al. 2014). In terrestrial ecosystems, soil is the main repository of heavy metal contaminants. Similarly, in aquatic systems, the sediment serves as the ultimate sink for these metals. The origin of such metals in the natural environment is from either geogenic or anthropogenic release, which causes interference or contamination on the aquatic and terrestrial food chains of humans and animals. Environmental contamination sources include mining wastes, landfill leachates, municipal wastewaters, urban runoffs, and industrial wastewaters, particularly from the electroplating, electronic, and metal-finishing industries. In addition, heavy metals are used in electronics, machines, and the artifacts of daily life; high-technology applications are also extensive (Ravindra et al. 2013). Such usage of heavy metals for advance technology results in the prevalence of emitted metal concentrations in the environment due to improper waste disposal. Therefore, high metal concentrations contaminate aquatic environments and cause harm to aquatic organisms and humans. Heavy metals tend to bioaccumulate in the food chain.

3.1 Sources of heavy metals as contaminants in soil

When soil is contaminated with metal, the effect can be malignant, especially on soil microbial properties (Yang et al. 2012) and soil diversity with respect to taxonomy and functionality (Vacca et al. 2012). The environmental/human risk associated with metal pollution cannot be overemphasized, with consideration of biomagnification tendencies (Roy and McDonald 2014). Some natural processes, such as land erosion, chemical weathering of minerals, and volcanic-associated activities, significantly contribute metals to soil and cause pollution. According to Abioye (2011), the heavy-metal-induced environmental pollution results from diverse human socioeconomic and development activities, such as mining, fuel and energy generation, wastewater disposal, and treatment. Khan et al. (2008) and Zhang et al. (2010) stated that such pollution can be due to various activities geared toward industrialization; hence, the pollutants come from waste disposal, lead-induced gasoline and paints, petrochemical spills, residues from incomplete combustion of coal, and atmospheric deposition.
Table 3 provides a summary of the various sources of heavy metals contaminating soil annually. Table 4 shows the heavy metal concentrations in polluted soil of some countries. Four main characteristics of heavy metal contaminated soil are as follows. First, contaminants are widely distributed due to economic development, which contributes to global contamination. Yang and Sun (2009) indicated that two heavy metal contamination events are listed in the world top 10 environmental events. Second, strong metal latency occurs because metals are colorless, odorless, and difficult to notice unless frequent analyses are conducted. Third, heavy metal-contaminated soil is characterized with irreversibility and remediation hardness. Self-purification and dilution techniques work poorly on this type of contaminant. Some metal-contaminated soils need 100–200 years to remediate (Wood 1974). Complexity arises from heavy metal contamination where more than one heavy metal contaminates the system. According to Emenike et al. (2014), more than 10 metals contaminate Malaysian landfill soils, thereby contributing to the complexity in the remediation process.
3.2 Sources of heavy metals as contaminants in air
Atmospheric metal deposition may be from a variety of sources, but many are linked to gas and dust. This contamination easily occurs from transportation sources, such as when items are carried with trucks and buses. Similarly, stationary sources of metals, such as factories, refineries, and power plants, deposit heavy metals to the atmosphere. Other sources may include indoor sources, such as construction materials and cleaning solvents, and volcanic-associated activities, which are classified as natural sources. For example, the average copper concentration in air in Jordan varies from 0.26 g/m$^3$ to 0.60 g/m$^3$, which is less than the concentration found in Riyadh but higher than those found in Taiwan, Cairo, Chile, and Spain. Lead pollution that occurs in downtown Central Sweden is mainly due to the urban industrialization of copper plants, sulfuric acid plants, and paint factories and the waste from mining and chemical industries. Pollution is transported by wind from the industrial waste to the surroundings.

3.3 Sources of heavy metals as contaminants in water
Heavy metal contamination in water can originate from untreated sewage and other wastewater types from chemical industries and urban mining. Activities, such as mining and construction, add high heavy metal concentrations to immediate water sources, especially ground water. Table 5 presents the heavy metal and source of contaminants in drinking water (EPA 2014). Some mature fruit orchards may contain high levels of arsenic, which was previously used as a pesticide. At high levels, these metals pose health risks. Lake waters and other forms of surface water naturally contain some concentrations of heavy metals at appreciable levels required for maintaining ecological equilibrium. Unfortunately, activities causing pollution change this ecological equilibrium. The varied effects of anthropogenic inputs from the natural inputs should be understood to enhance environmental management.

Ground water contamination is caused by leachates from landfills generated decades ago (Hem 1989; Butow et al. 1989; Alloway and Ayres 1997). Leachate contains different types and concentrations of heavy metals. In the urban area of Nigeria, the groundwater generally contains Cu (0.02 ± 0.04 mg/L), Fe (4.23 ± 6.4 mg/L), Pb (2.4 ± 3.3 mg/L), and Co (1.03 ± 1.1 mg/L). Accordingly, these concentrations are above the permissible limits recommended by the World.
Health Organization (0.5, 0.1, 0.01, and 0.0002 mg/L, respectively), and the distance from ground water to landfill is 2 km (Oyekul and Eludoyin 2010). Metals also cause incessant contamination of ground water. Given the industrial metal pollution in the valley of River Po in North Italy, the underground water source is rendered useless because it is permanently closed. Pollutants may permeate the environment gradually at small concentrations, but toxic effects may be amplified due to bioavailability and accumulation with the entry of the pollutants (heavy metals) into the food chain. Metal pollution is often confined at a specific location, but borderless distribution may be possible due to the economic importance of metals. Metals were used even before the Industrial Revolution, and it remains a core component of most production. Hence, the global distribution of metal pollution should be elucidated to show the need for reclamation.

4.0 GEOGRAPHICAL OUTLOOK OF HEAVY METAL-POLLUTED SOIL

4.1 Asia

Asian countries, especially China, Thailand, Japan, Korea, and India, engage significantly in agriculture, which involves rice cultivation. Thus, the surface layer of certain rice paddy soils in Korea contains Cd, Cu, Pb, and Zn, with a level ranging from 0.11 mg kg\(^{-1}\) to 4.47 mg kg\(^{-1}\) (Jo and Koh 2004). Similarly, the same metals are almost 20 times (75.9 mg kg\(^{-1}\)) higher in the rice fields of Japan. Furthermore, China, where metal pollution causes soil contamination problems with 446 mg kg\(^{-1}\) average levels of Cd, Cu, and Zn in rice fields, exhibits the worst condition among the studied sites (Luo and Teng 2006; Brus et al. 2009). Norra et al. (2005) reported that 0.7 mg kg\(^{-1}\) As is detected in the winter wheat of west Bengal Delta Plain due to irrigation with As-rich groundwater. The level of toxic heavy metals in the wastewater of China is high. Approximately 8 million acres of polluted farmland in China and 13 million tons of crops harvested annually are contaminated with heavy metals. Guangdong Province officials discovered excessive levels of Cd in 155 batches of rice collected from markets, restaurants, and storehouses. Additionally, 89 out of these 155 batches of collected rice are from Hunan Province. Hunan Province is the top producer of nonferrous metals, which makes this area the leading source of pollutants (Cd, Cr, Pb, and As), according to the data collected from 2011 by the Institute of Public and Environmental Affairs of Beijing (2011). The large earthquake on the eastern coast of Japan in 2011 caused nuclear accidents, which affected the soil and agricultural
products. Rapid industrialization in Japan causes dangerous level of heavy metal pollution in soil; Cd exerts the most detrimental effect in Japan and causes a disease called Itai Itai disease (Tomoyuki 2010). This disease is characterized with renal insufficiency and painful bones, which are secondary to osteomalacia. Chronic Cd toxicity, combined with malnutrition, is an etiologic factor.

4.2 Africa

Urbanization and other industry-related activities contribute to the large waste generation in Africa, and heavy metals are common components of the waste stream. Historically, mining is common to Africa, and it causes leaching of metals, especially in Algeria (Hg), Namibia (As), South Africa (As), Nigeria (Sn), Democratic Republic of Congo (Sn), and Zambia (Cu). However, mining is not the sole cause of metal pollution in Africa; other commercialization subsistence practices, such as electroplating, leather tanning, vehicular emissions, oil and gas explorations, effluent discharge from powerlines, intensive agriculture, and sludge disposal, are also significant contributors. Critical evaluation of metal pollution in Africa showed that Nigeria possesses a widespread distribution of Pb and other metals that contaminate soil, water courses, atmosphere, and the rich vegetation, thereby significantly impairing human health. The awareness level about heavy metals is considerably low, especially for Cd, Cr, and Hg. Dust samples obtained from streets present high Cd levels; these samples are exposed to high traffic due to dense populations.

To improve the agricultural productivity and eliminate crop pests, fertilizers and pesticides are commonly used in Nigeria. This country imported about one billion tons of commercial fertilizers in 1983, and the heavy metal contents of these fertilizers are unknown. Fertilizers may contain approximately 400 mg kg\(^{-1}\) Pb, which may constitute a major source of soil pollution, although phosphate lead (PbSO\(_4\)) is not often readily available to plants (Nriagu 1978). Phosphate fertilizers also contain Cd, which can be a contaminant in agricultural land and crops. An important problem associated with tropical weathering that presents considerable implications on soil susceptibility to pollution is acid soil development with low-buffering capacities. Such soils lack one or more nutrients due to leaching, soil erosion, and extractive farming practices. Soil acidity promotes sorption of toxic metals in both plants and soils and involves high levels of soluble Al. The Republic of Zambia is rich with mineral resources, such
as Cu, Co, Zn, and Pb (Stockwell et al. 2001), and mining is the most established industry. Stockwell et al. (2001) stated that approximately 3% of the world’s yearly Cu production and the annual production of 20% in 1997 both come from Zambia, where ores are smelted. The core mining areas in Zambia are Kabwe town and Copperbelt. Hence, heavy metal pollution is considered one of the most important environmental issues in Zambia, and this pollution causes severe effects on humans and animals (Nwanko and Elinder 1979; Syakalima et al. 2001). Given the transportation of mined metals through waterways, the pollution levels at nearby rivers and sediments are high in Cu and Pb concentrations. However, in areas geographically distant from the mines, heavy metal concentrations are moderate or low.

### 4.3 United States of America

As one example of the issues facing North America, in the USA alone, 600,000 contaminated brownfields are identified that require an appropriate remediation method (McKeenan 2000). According to the US government data, coal mines contaminate more than 19,000 km of US stream water with heavy metals. Additionally, about 100,000 or more croplands are damaged due to the considerable level of metal contamination (Ragnars Dottir and Hawkins 2005). Soil contamination is one of the major reasons of the enforced critical monitoring for heavy metals in drinking water to ensure safe consumption in the USA; metal concentrations must be kept at a safe limit or maximum contaminant level based on standards from the Environmental Protection Agency. High-level metal contamination is widespread in Boston Harbor, San Francisco Bay, and Long Island Sound, and such sedimentary basins will remain polluted for decades. Small portions of the basin sediments (metal bound) re-enter the water, and they are occasionally transformed into remarkably detrimental forms (U.S Department of Labor 2014).

### 4.4 Europe

Industrial activities are responsible for over 60% of Europe’s soil pollution (heavy metals account for 37% of the total). The European Environment Agency approximated that more than 250,000 soil-polluted sites exist in Europe, with about 80,000 cleanups across the EU countries in the last 30 years. The most contaminated soils are those close to waste landfills, oil and gas facilities, industries, military stations, and nuclear power plants. The economic activities in European society generates additional system wastes, and over 90 million tons from the 3 billion tons of generated solid wastes are hazardous. The Environmental Data Centre on waste-specific
evaluation revealed that contemporary Bulgarian agriculture is facing threats due to natural irregularities over the past decades. The consequent economic difficulties and anthropogenic influences mainly consist of soil contamination and poor farmer practices. Contaminations from Cd, Zn, Pb, and As, and operations from diverse nonferrous factories polluted approximately 200,000 ha soils in Bulgaria with the same metals at levels above the maximum limit (Atanasov et al. 1993; Dinev 1998, Dinev et al. 2008). This kind of contamination can cause adverse effects on human health (Adriano et al. 2004). In Poland, 0.5% of the total soil is contaminated with metal. In France, approximately 800,000 sites are exposed to similar conditions. Metal contamination in Armenia results in a number of crop yield issues, plant toxicities, and Cd and Pb accumulations. The atmospheric Pb level of Yerevan is 1.2–1.3 of the maximum allowable concentration (MAC); in highways, the level is 16–19 MAC (Jugaryan 2000). Other Armenian cities, such as Vanadzor, have an atmospheric Pb concentration that is 15–20 times higher than the MAC standard. Alaverdi is a mining town with 10-fold higher contamination than the MAC standard. The Pb content of most crops obtained from contaminated areas near Alaverdi is 25 times more than the MAC standard; apples and peaches are 15 and 5 times more contaminated, respectively. Despite the significant Pb exposure incidence, the associated public health issue remains significantly unexplored. During the investigation on the blood lead level in the Republic of Armenia in 1996, more than 300 workers responded within four establishments; varying conditions of Pb absorption (low to moderate) characterized the study on Armenian children living in the Yerevan districts between 1992 and 1995. Furthermore, 923–7692 Cd coefficients are contained in solid waste, especially in the slag and dust flow from the combination of Alaverdi mining and metallurgy in 1992 (Jugaryan 2000).

For the reasons outlined above, remediation technologies are necessary for the recovery of metal-contaminated environment and prevention of continuous environmentally toxic impact on living organisms. Various chemical and physical methods adopted in the past are not economically viable, and they do not ensure restoration without residual effects. Natural processes utilizing plants (phytoremediation) and microorganisms (bioremediation) can remove or reduce environmental pollutants, including metals, at various levels (Abioye et al. 2011; Emenike et al. 2016).
**5.0 PHYTOREMEDIATION**

Phytoremediation is a considerably promising method for the removal of pollutants from the environment. Plants significantly concentrate elements and compounds from the environment and consequently induce molecular metabolism within tissues (Garbisu and Alkorta 2003). Raskin and Ensley (2000) and Tyler et al. (1989) viewed the technology as a major environmental cleanup option that utilizes specialized plants, which are also engineered to accumulate pollutants. The remediation process from plants is distinct; various parts of the plant tend to follow specific mechanisms of action, such as uptake by root systems, translocation through the designated tissues, bioaccumulation and eventual storage of pollutants, or degradation within the other plant parts. These mechanisms explain the association of plants with the microbial rhizosphere and cause the sequestration, degradation, or immobilization of pollutants in soil as a cleanup option and in water matrices (contaminated with heavy metal) (Pilon 2005).

The above process takes into account several factors, namely, changes in plant species, development stages of the plants, and characteristics of metals that control the extent of absorption, accumulation, and translocation (Nouri et al. 2009). Several current practices for metal remediation in soil fail to address discretely the contamination problem due to the digging, dumping, and encapsulation activities involved. Immobilization or extraction techniques can be largely expensive, whereas phytoremediation is inexpensive (Paz et al. 2014). Phytoremediation displays a significant advantage, especially with respect to reduced cost over other physicochemical remediation technologies. Phytoremediation is easily practiced *in situ*, and the use of solar energy promotes functional processes that require little or no maintenance once initiated. Hence, the market trend for phytoremediation is rapidly increasing, especially in the US, which produces $100–150 million per year (Vinita Hooda 2007). Phytoremediation is environmentally friendly, and can potentially control erosion or contaminant leaching from the polluted areas. This process also reduces the exposure of polluted substrates to humans, wildlife, and the environment (Pilon 2005). The success of phytoremediation on metal-contaminated soil is evident at some military, industrial, and agricultural stations and fields (Banuelos 2000; Winter Sydnor and Redente 2002). Certain limitations in phytoremediation, especially locations and climatic situations that easily influence the site to be cleaned, temperature, altitude, soil type,
and ease of moving agricultural equipment, should be considered (Schmoger et al. 2000). Furthermore, pH, organic matter, cation exchange capacity of soil, plant species, and cultivars and age of plant can affect the uptake of heavy metals by plants (Rosseli et al. 2003). More than 400 species of metal hyperaccumulators are from both terrestrial and wetland plants (Baker et al. 2000; Zhao et al. 2001; Yoon et al. 2006). Ebbs et al. (1997) carried out metal accumulation trial on 30 plant species in hydroponics for 4 weeks; their results indicated that many *Brassica* spp., such as *B. juncea* L., *B. juncea* L. Czern, *B. napus* L., and *B. rapa* L., exhibit moderately enhanced Zn and Cd accumulation. Plants with high biomass, such as willow, are involved in phytoremediation (Landberg and Greger 1996); plants with low biomass that possess hyperaccumulating potentials, especially *Thlaspi* and *Arabidopsis* species, are also involved in this mechanism. The number of plant species with hyperaccumulation capability for metal concentration at levels higher than 1000 mg/kg dry weight is 4 (As), 14 (Pb), 1 (Cd), >320 (Ni), 34 (Co), 20 (Se), and 34 (Cu) (Reeves 2003). In phytoremediation, several strategies are involved. Table 6 shows the five main strategies involved in phytoremediation.

### 5.1 Case practices in phytoremediation

#### 5.1.1 Removal of heavy metals from wetlands

Wetlands are important sinks for heavy metals, and they can exert toxic effects on biota (Keller et al. 1998). In riparian wetlands, heavy metals exist mainly in water, soils, and biota. Hence, riparian wetlands can accumulate a large amount of heavy metals (Lejeune et al. 1996; Prokisch et al. 2009). Wetlands are affected rapidly because of growing urbanization coupled with industrialization. In developing countries, industrialization occurs through the replacement of natural ecosystems, with the main objective of commodity production for a short–term benefit. Consequently, industrial colonies are developed, and urban wastes are dumped in the altered environmental setups. Heavy metal pollution causes considerable acidity of land, and high metal content alters the biotic community composition, which can result in mortality. Naturally, wetlands can tolerate metal to some extent, but once it becomes saturated it will have the potential to cause environmental problems. Heavy metals normally enter the environment through a network of different canals and channels that adversely affect aquatic organisms after deposition. Water hyacinth (*Eichhornia crassipes* Mart. Solms) was studied for its ability to take up and translocate metals from Erh–Chung wetlands in Taiwan. The potential of water hyacinth
to translocate metals is in the order of Zn < Ni < Cd < Ni < Zn. Water hyacinth presents bioconcentration abilities when planted in aquatic environments with low concentrations of the selected metals. The plant roots accumulate metal concentrations that are more than 3–15 times higher than concentrations accumulated in the shoots. Hence, the order of absorption in terms of concentration at the roots of the plant is Cu > Zn > Ni > Pb > Cd. Moreover, the absorption capacity of water hyacinth is 0.24, 5.42, 21.62, 26.17, and 13.46 kg/ha for Cd, Pb, Cu, Zn, and Ni, respectively. The phytoremediation potential of water hyacinth is significant, and it can remove Cd, Cu, Pb, and Zn from wastewater (Shao and Wen 2004).

5.1.2 Removal of heavy metals from previous mining lands

Removal of heavy metals from soil with plants (phytoremediation) on land affected by tin mining was studied by Muhammad Aqeel Ashraf et al. (2012). The tin tailing area is located at a previous tin mining site in Bestari Jaya, Kuala Selangor. This area covers 8 ha with sandy soil texture. Previous experiments used nine plant species for the evaluation of plant phytoextraction abilities for the reduction of metals (Pb, Cu, Zn, As, and Sn) from contaminated tailings; these species include *Cyperus rotundus* L., *Imperata cylindrica*, *Lycopodium cernuum*, *Melastoma malabathricum*, *Mimosa pudica* Linn, *Nelumbo nucifera*, *Phragmites* L., *Pteris vittata* L., and *Salvinia molesta*. According to quantity (dry weight) accumulated by each plant, their findings indicated that *C. rotundus* L., *I. cylindrica*, *N. nucifera*, *Phragmites australis* L., and *P. vittata* L. accumulate 658, 245, 288, 345, and 278 mg kg\(^{-1}\) metals, and their bioconcentration factors are approximately 0.40, 0.32, 0.57, 0.71, and 0.65, respectively. The phytoextraction rates are 86%, 42%, 56%, 49%, and 31% for Sn, Zn, As, Cu, and Pb, respectively. These plant species exhibit potential for successful phytoremediation of tin mining tailings in Peninsular Malaysia.

5.1.3 Removal of heavy metals from agricultural soils

Metal pollution in Taiwan paddy soils is a significant problem that involves illegal disposal of wastewater from industries, mainly chemical and electroplate plants, rather than only metals from parent materials (Chen 1992). An important example is the extent of Cd contamination induced by plastic stabilizer that is used to produce rice in Taoyuon, Taiwan in the 1980s. During this period, about 100 ha of paddy fields are contaminated with excess Cd and Pb due to the illegal discharge at a location proximal to the field (Chen 1991). Farmers discovered that rice plants were visibly affected; the leaves demonstrated brown spots, rice grains were affected with
chlorosis, and the whole plant prematurely died prior to harvest. Further investigation showed that more than 10 and 0.5 mg kg\(^{-1}\) Cd are stored in the soils and rice tissues, respectively. Such incidents significantly influence the Taiwanese environment. In northern Taiwan, another large-scale phytoextraction study on paddy soil contaminated with Cd was conducted (Chen and Lee 1997). Eight flower species, namely, *Rhododendron* spp., *Osmanthus* spp., *Pentas lanceolata*, *Salvia splendens*, *Cosmos bipinnatus*, *Zinnia elegans*, *Celosia argentea*, and *Verbena tenera*, were planted on a polluted site to understand phytoextraction. Results of the above experiment showed that *C. argentea*, *P. lanceolata*, and *V. tenera* accumulate high Cd concentration levels. These plants can accumulate 30–40-fold higher Cd concentrations than that of the initial levels found in plant tissues. Scarlet sage, common cosmos, and zinnia increase the accumulation by approximately 10-fold compared with the initial concentration of Cd in plant tissues. *Osmanthus* and azalea plants absorb low amounts of Cd (2–4 mg kg\(^{-1}\)). Cd accumulation in different plant samples are shown in Table 7.

Another study on phytoremediation was conducted in 2006 at a heavy metal-contaminated field located in Changhua, central Taiwan. The contaminated area (1.3 ha) was mostly polluted with Cr, Cu, Ni, and Zn. This site was used to conduct a feasibility study on phytoremediation in Taiwan (Lai et al. 2009). Twelve plant species were used. The preliminary results showed that, within the first 31 days of growing on this contaminated site, most of the plant species accumulate significant amounts of metal in their shoots. This preliminary experiment also revealed that the plants accumulate high concentrations of metals in their shoots in the following order: garden canna and garden verbena (45–60 mg Cr kg\(^{-1}\)), Chinese ixora and kalanchoe (30 mg Cu kg\(^{-1}\)), rainbow pink and sunflower (30 mg Ni kg\(^{-1}\)), and French marigold and sunflower (300–470 mg Zn kg\(^{-1}\)). Plant roots tend to accumulate higher concentrations of heavy metals than those of the shoots. The phytoavailability of soil metals decreases with time during phytoextraction, which increases the period required for effective remediation. Figure 1 illustrates the uptake mechanisms of phytoremediation technology. Phytoremediation requires 3–20 years to reduce the immediate concentrations of Cr, Cu, Ni, and Zn to the regulated levels based on the Soil and Groundwater Pollution Remediation Act of Taiwan. Results of this feasibility study also showed that the use of suitable plants contaminated with high concentrations of heavy metals enabled the contaminated sites to recover to their natural
condition and generate economic benefit (Zeng et al. 2010). Table 8 provides a list of metal pollutant-accumulating plants.

6.0 MICROBIAL BIOREMEDIATION

Heavy metals cannot be degraded, but they can be transformed from one oxidation state to another inorganic complex. This transition can be achieved by a microbial remediation method. According to their effect on the environment and human health, bioremediation is one of the most feasible methods for the remediation of soil that is contaminated with organic and inorganic compounds. This process utilizes microorganisms or plants to decontaminate or remove organic and inorganic xenobiotics from the environment. Bioremediation is an environmentally friendly technology solution to overcome heavy metal contamination. This method is a sustainable remediation technology that rectifies and re-establishes the natural soil condition. Bioremediation is also listed among new technologies or approaches that derive its scientific justification from the emerging concept of environmentally friendly chemistry and engineering. This technology is a fast growing and promising remediation option that is increasingly studied and applied for pollutant cleanup (Dadrasnia et al. 2014). The response of microbial communities to heavy metals relies on the concentration and availability of metal ions. The microbe reaction to metal is a remarkably complex process, which is controlled by several factors, such as type of metal, nature of medium, and microbial species, when active uptake of heavy metals (bioaccumulation) and/or passive uptake (adsorption) occurs. Microbial cell walls, which mainly consist of polysaccharides, lipids, and proteins, offer many functional groups, including carboxylate, hydroxyl, amino, and phosphate, which can bind heavy metal ions. Bioremediation is possible in soil, sediment, and water through biological process, and it can be practiced ex situ or in situ. Ex situ technologies are treatments carried out physically for the removal of contaminant in another area (possibly within the site) for final treatment, whereas in situ techniques involve the treatment of contaminated material in its immediate location. Several factors influence the bioremediation process: i) loss of microbial viability during inoculation (Van Veen et al. 1997), ii) eventual cell death after inoculation (Liu et al. 2009), iii) competition (Thompson et al. 2005), iv) predation (Bouchez et al. 2000), v) pH (Dibble and Bartha 1979), vi) temperature (Atlas 1981), and vii) moisture (Leany and Colwell 1990).
Heavy metals do not go through chemical or biological degradation to alter or reduce their toxicity over time (Knox et al. 2000). The microorganisms involved in bioremediation cannot degrade the metal, but they can transform it from one oxidation state or organic complex to another state. During effective bioremediation processes, the metal can be transformed to either a water-soluble, low toxic state or to a low water-soluble state; thus, the metal precipitates and becomes less bioavailable, or it is removed from the contaminated site or volatilized and removed from the polluted area (Garbisu and Alkorta 1997). Microbes tend to decrease some metals in metabolic processes enzymatically; these metals do not involve metal assimilation (Lovley et al. 1993). Several bacteria couple the oxidation of simple organic acids and alcohols, hydrogens, or aromatic compounds.

An example of heavy metal bioremediation is when all bacteria species essentially need $\text{Fe}^{3+}$, and $\text{Fe}^{2+}$ is important only for anaerobic bacteria (Ahemad 2014). Heavy metal adsorption by microbes depends on the total biomass of the microbes and geochemistry of the whole system. Nanda and Abraham (2011) studied the effects of Cu, As, Cr, and Mg on some essential soil bacteria, such as \textit{Azotobacter}, \textit{Pseudomonas}, and \textit{Rhizobium}; they found that As is the most toxic among the studied metals. The survival of microbes under metal stress involves several mechanisms, which include the efflux of metal ions outside the cell, accumulation and development of complex metal ions inside the cell, and eventual decrease of the toxic metal to non-toxic state. The microorganisms involved in this process can be bacteria, fungi, yeast, and algae. Potent metal-tolerant bacteria include \textit{Bacillus} sp., \textit{Pseudomonas} sp., \textit{Streptomyces} sp., and \textit{Pseudomonas aeruginosa} (Tunali et al. 2006; Uslu and Tanyol 2006; Soltan 2001). Fungus biomasses are effective among microorganisms due to the high percentage of cell wall material and excellent metal-binding capacity. \textit{Aspergillus} sp., \textit{Streptoverticillum} sp., and \textit{Sacchromyces} sp. are examples of fungi/yeast with high levels of biosorption potential (Puranik and Paknikar 1997). Heavy metal removal through microbial remediation can be achieved through several approaches, such as bioaugmentation, biostimulation, and bioattenuation.

\section*{6.1 Bioaugmentation}

Bioaugmentation is used to improve the degradation activities of contaminated sites by introducing specific potential microbes or groups of microorganisms. The bioaugmentation method efficiency is influenced with many abiotic and biotic factors (Agnieszka and Zofia
Bioaugmentation involves the application of indigenous bacteria to contaminated sites to accelerate the removal of undesired compounds. According to Forsyth et al. (1995), bioaugmentation is mainly suitable for soils with considerably low levels of contaminant-degrading microbes and those with compounds requiring multi-process remediation, including processes that are detrimental or toxic to microbes and suitable for small-scale sites; the cost of nonbiological methods exceeds that of bioaugmentation. In many contaminated soils, the microorganisms remain exposed to various chemicals with additive, synergistic, or antagonistic effects (Chaperon and Sauve 2008). Laboratory studies demonstrated significantly reduced metal concentrations in polluted soil through the use of bioaugmentation (Emenike et al. 2016; Emenike et al. 2017, Fauziah et al. 2017).

6.2 Biostimulation

Biostimulation is a process where the environment is modified to stimulate the existing bacteria, which can enhance bioremediation. This process can be carried out by adding nutrients, such as phosphorus, nitrogen, oxygen, or carbon. Nutrient addition aims to increase the population or activity of naturally occurring microorganisms available for bioremediation. The advantage of the biostimulation method is that the native microbes present induce bioremediation due to adaptation to the subsurface environment and optimal spatial distribution within the subsurface. Some factors that may limit the activity of biostimulation in soil for heavy metal removal are nutrients, pH, temperature, moisture, oxygen, soil properties, and contaminant type (Atagana 2008, Al Sulaimani 2010; Bundy et al. 2002). Fulekar et al. (2012) carried out a biostimulation study using bacteria cultured from isolated heavy metals, which were obtained from a contaminated site located at Bhayander (east), Mumbai, India. Metal-tolerant bacteria were isolated and introduced into bioreactor with selected metals, namely, Fe, Cu, and Cd, at different concentrations (25, 50, and 100 µg/mL, respectively). The experiment was biostimulated under aerobic conditions to induce the bioremediation of heavy metals. The biostimulated bacterial consortium was effective in the removal of high concentrations of Cd, Cu, and Fe (approximately 98.5%, 99.6%, and 100%, respectively) at a rate of 100 mg/L. Fe can be completely remediated in this study. Kanmani et al. (2012) also performed biostimulation for Cr removal by using heterogeneous groups of bacteria isolated from contaminated sites. Kanmani et al. (2012) indicated that the isolated bacteria exhibited plasmid-mediated chromate
resistance, and the reduction was enzymatically mediated. It is possible that high-performance bacteria can be obtained at extreme conditions with the use of genetic engineering technology.

6.3 Bioattenuation

Bioattenuation is another in situ treatment method adopted for microbial remediation of heavy metals. This method utilizes natural processes to control the spread of contamination from chemical spills and decrease the concentration of pollutants at contaminated sites. Consequently, the environmental contaminants remain undisturbed to provide an opportunity for natural degradation, reduction, or transformation of the contaminant. Natural attenuation is a part of a site cleanup, and it also includes the control or removal of the source of contamination. The effectiveness of bioattenuation typically depends on activities prevalent at the polluted sites. Nonetheless, the bioattenuation rate varies due to the types of pollutants and associated physical, chemical, and biological characteristics of the soil and ground water. This process may reduce contaminant mass (biodegradation and chemical transformations) by reducing the concentration of pollutants (through simple dilution or dispersion) or binding contaminants to soil particles so that the contamination will not spread or migrate distantly (adsorption). This process is an effective, inexpensive, and the most appropriate method to remediate contamination problems. Bioattenuation depends on natural processes to dissipate contaminants through biological transformation.

6.4 Case study on bioremediation

Europeans have invested large amounts of money to remediate contaminated soils. In the 1980s, the U.S. Congress passed the Comprehensive Environmental Response, Compensation and Liability Act for the protection of human health and remediation of environmental pollution. Resource Conservation and Recovery Act and Superfund Amendment and Reauthorization Act are also involved and focused on the standard and behavior of soil remediation. In the period of 1982–2002, the total remediated land area in Europe was approximately 18.35 million m³. Great Britain also passed the Environmental Protection Act in the 1990s, in which the second part clearly stated the principle of polluter responsibility (Zhitong et al. 2012). The sewage irrigation areas in China are about 1400 km², but more than 60% of this area is polluted with heavy metals. According to the USEPA (1997), more than 200,000 heavy metal contaminated sites in US require cleanup to protect human health and the environment (Krishna et al. 2010).
6.4.1 Bioremediation of heavy metal-contaminated soil in wetlands

In a case study by Srabanti Basu et al. (2014) on chromium remediation in East Calcutta wetlands, bioremediation was considered a good solution. The major sewage treatment plant, which is located in the East Calcutta Wetlands (previously known as Calcutta), is contaminated with several heavy metals. Their study focused on the possibility of bacterial isolation from the sites to tolerate chromium (VI). Bacillus subtilis was isolated and studied for potential tolerance toward chromium (VI) at a concentration of 2.5–7.55 µg/L; this organism reduced about 97% and 90% of residual chromium concentration after 24 h, with initial concentrations of 2.5 and 5 µg/L, respectively. The highest activity was observed at 30 °C. The growth of the Bacillus sp. strain in the presence of chromium (VI) was best fit for Tessier model (the growth rate of microorganisms). Bacillus strain can complete or improve the removal treatment of chromium (VI).

6.4.2 Bioremediation of heavy metal-contaminated soil in previous mining sites

Mining and smelting activities have largely contributed to soil contamination and poses high risks to human and ecological health. A total of 20,000,000 acres of farmland in China are contaminated with different types of heavy metals, and this area accounts for one-fifth of the total arable farmland. The quality of soil in farmlands surrounding the mining site became poor; the heavy metal level already exceeds the third level of environmental quality standard for soil in China (GB15618-1995). Bao Chen et al. (2011) used two Pb–resistant bacteria, namely Bacillus pumilus and P. aeruginosa (GeneBank accession Nos. FJ402988 and GU017676); these bacteria were isolated and identified from the soil of a Pb-mining district (Heilongjiang province, China) based on the 16S rDNA gene sequence analysis. The bacteria were inoculated into soil planted with cabbages at different Pb concentrations. To understand the remediation potential of isolated bacteria, several indices, including microbial count, soil enzyme activity, microbial community diversity, and soil Pb concentration, were investigated. Results indicated that the bacterial count in 1000 mg/kg Pb-treated soil was largely affected with inoculation of Pb-resistant bacteria; the count increased by about 237% and 347% over that of the control without bacterial addition. Microbial community diversity was also analyzed by polymerase chain reaction–denaturing
gradient gel electrophoresis (DGGE). Results proved that the samples inoculated with Pb-resistant bacteria exhibit more bands and higher intensities in DGGE patterns than those of uninoculated samples. For samples inoculated with Pb-resistant bacteria, the reduction of Pb concentration in rhizospheric soil was at least 15 mg/kg and 42 mg/kg at most. In conclusion, *P. aeruginosa* exhibits an excellent tolerance to high Pb concentration and strong remediation ability.

### 6.4.3 Bioremediation of heavy metal-contaminated soil in agricultural soil

Meghraj and Daneshwar (2013) successfully isolated heavy metal-tolerant bacteria from industrial and agricultural areas in Mauritius. These bacteria evolve their uptake and efflux mechanisms to adapt in heavy metal-contaminated environments and represent a potential source for bioremediation processes. They isolated approximately 113 bacteria that significantly grow and survive in Hg, Pb, Zn, and Cu solutions at different concentrations (0.5–5.0 mM). Strains were identified by biochemical tests. 16S rRNA gene sequence analysis revealed that all of the strains belong to Bacillales.

### 6.4.4 Bioremediation of heavy metal-contaminated soil in residential areas

Diels et al. (1999) reported that many geographical areas in Europe are affected with emissions of old nonferrous factories. About 50 sites in Europe are contaminated with different types of metals, including Zn, Cd, Cu, and Pb. *Alcaligenes eutrophus* CH34 is used in this study for metal remediation through metal solubilization by biocrystallization capacity method. The bacteria can solubilize metals through the production of siderophores and adsorb the metals in biomass on metal–induced outer membrane proteins by bioprecipitation. When bacteria are added to soil, the metals move toward the biomass. The biomass was separated through flocculation processes. The Cd concentration in sandy soils decreased by approximately 85%. Similarly, Zn was reduced from 1070 mg/kg to 172 mg/kg, which is about 84% reduction. The lead concentration also decreased from 459 mg/kg to 74 mg/kg. Biosensors were used to measure a complete decrease in the bioavailability of metals.

In China, many sewage irrigation areas experience a reduced agricultural yield due to heavy metal pollution, especially Cd. Jiang and Fan (2008) evaluated the potential of sulfate-reducing bacteria (SRB) for bioremediation of Cd–contaminated soil. They used the Tessier
sequential extraction method for the geochemical speciation of metal Cd using SRB. Results revealed that SRB can reduce the Cd concentrations, which can be easily absorbed by plants. The removal efficiency is about 70%. Addition of SRB to water-logged soils is later measured for Cd speciation for every 7 days in a span of 33 days. During this period, the total Cd concentrations remain unchanged. However, the Cd form changed significantly. The concentrations of the exchangeable Cd fractions were reduced significantly, which indicated that Cd bioavailability in the soils was markedly decreased. The concentrations of the Fe–Mn oxide fraction of Cd increased remarkably from 60% to 120%. The concentrations of the carbonate and organic matter fractions of Cd also increased slightly. The oxidation–reduction potential ranges from −450 mv to 150 mV. The rate of sulfate reduction decreased with the increased total Cd concentration.

7.0 CONCLUSIONS

Contaminated environments have become common and are of global concern due to their ecosystem impact and associated socioeconomic loss. The adoption of biological approaches aids in environmental restoration, and is also environmentally resilient. Microbial and enzymatic activities in heavy metal-contaminated soil are often inhibited. Microbial biomass is reduced with contamination. Inhibited cytoplastic enzymes and damaged cell structures are caused by oxidative stress occurring in plants due to heavy metal contamination. More than 400 species of metal hyperaccumulators are from both terrestrial and wetlands plants. Microbial cell walls, which mainly consist of polysaccharides, lipids, and proteins, offer many functional groups, such as carboxylate, hydroxyl, amino, and phosphate, which can bind heavy metal ions. The most remarkable biotransformation technologies suitable for plant remediation of metal-polluted soils include phytotransformation, phytostimulation, phytoextraction, phytostabilization, and phytovolatilization. Bioaugmentation and biostimulation are the most suitable methods for microbial restoration of metal-polluted environments, whereas bioattenuation is perhaps the least suitable technique because of time constraints. Established case studies revealed that biotransformation and removal of heavy metals will aid in the restoration of polluted wetlands, ex-mining lands, agricultural soils, and residential areas. These approaches are recommended for field use, where industrialization and rapid economic development cause environmental deterioration.
8.0 ACKNOWLEDGMENTS

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9.0 REFERENCES


Figure Captions

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<th>Caption</th>
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<tr>
<td>1.</td>
<td>Figure 1. Uptake mechanisms of phytoremediation technology (Interstate Technology and Regulatory Council 2009)</td>
<td>This indicates intrinsic process involved in use of plants for remediation purpose. It shows various processes that may take place when plant root comes into contact with the pollutant of interest.</td>
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Figure 1: Uptake mechanisms of phytoremediation technology (Interstate Technology and Regulatory Council 2009)

76x98mm (300 x 300 DPI)
Table 1. Effect of heavy metals on plants (Ann, 2005)

<table>
<thead>
<tr>
<th>Types of heavy metals</th>
<th>Effects of heavy metals on plants</th>
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<tbody>
<tr>
<td>Chromium</td>
<td>Reduces the rate of photosynthesis and enzyme activity, damages the plant membrane and roots, and causes chlorosis</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Decreases seed germination, lipid content, and plant growth</td>
</tr>
<tr>
<td>Copper</td>
<td>Affects growth, reproductive processes, and photosynthesis of plants and decreases the thylakoid surface area</td>
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<tr>
<td>Mercury</td>
<td>Decreases photosynthetic activity, water uptake, and antioxidant enzymes</td>
</tr>
<tr>
<td>Nickel</td>
<td>Reduces seed germination and production of protein, chlorophyll, and enzyme</td>
</tr>
<tr>
<td>Lead</td>
<td>Reduces chlorophyll production and affects plant growth</td>
</tr>
<tr>
<td>Zinc</td>
<td>Reduces seed germination</td>
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Table 2. Toxic effects of excess concentrations of heavy metals on human health

<table>
<thead>
<tr>
<th>Heavy Metal</th>
<th>Environmental Protection Agency (EPA) Regulatory Limit (ppm)</th>
<th>Toxic Effects</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.10</td>
<td>May cause skin and other body tissues to turn grey or blue-gray and lead to breathing problems, lung and throat irritations, and stomach pain</td>
<td>ATSDR (1990)</td>
</tr>
<tr>
<td>As</td>
<td>0.01</td>
<td>Affects essential cellular processes, such as oxidative phosphorylation and ATP synthesis</td>
<td>Tripathi et al. (2007)</td>
</tr>
<tr>
<td>Ba</td>
<td>2.0</td>
<td>Causes cardiac arrhythmias, respiratory failure, gastrointestinal dysfunction, muscle twitching, and increased blood pressure</td>
<td>Acobs et al. (2002)</td>
</tr>
<tr>
<td>Cd</td>
<td>5.0</td>
<td>Carcinogenic, mutagenic, endocrine disruptor, causes lung damage and bone fragility, affects calcium regulation in biological systems</td>
<td>Salem et al. (2000), Degraeve (1981)</td>
</tr>
<tr>
<td>Cr</td>
<td>0.1</td>
<td>Causes hair loss</td>
<td>Salem et al. (2000)</td>
</tr>
<tr>
<td>Cu</td>
<td>1.3</td>
<td>Causes brain and kidney damage, liver cirrhosis, chronic anemia, and stomach and intestine irritations</td>
<td>Salem et al. (2000), Wvana and Okiemen (2011)</td>
</tr>
<tr>
<td>Hg</td>
<td>2.0</td>
<td>Causes autoimmune diseases, depression, drowsiness, fatigue, hair loss, insomnia, memory loss, restlessness, vision disturbance, tremors, temper outbursts, brain damage, and lung and kidney failures</td>
<td>Neustadt and Pieczenik (2007), Ainza et al. (2010), Gulati et al. (2010)</td>
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<tr>
<td>Ni</td>
<td>0.2</td>
<td>Causes skin allergies, such as itching; cancer of the lungs, nose, sinuses, and throat through continuous inhalation; immunotoxic; neurotoxic; genotoxic; affects fertility; causes hair loss</td>
<td>Salem et al. (2000), Khan et al. (2007), Das et al. (2008), Duda and Baszezyk (2008)</td>
</tr>
<tr>
<td>Pb</td>
<td>15</td>
<td>Excess exposure in children causes impaired development, reduced intelligence, short-term coordination problems, and risk of cardiovascular</td>
<td>Salem et al. (2000), Wyana and Okiemen (2011)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dietary exposure of approximately 300 µg/day affects endocrine function, impairs the natural killer cell activity, and causes hepatotoxicity and gastrointestinal disturbances</td>
<td></td>
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<td>---</td>
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<td></td>
</tr>
<tr>
<td><strong>Se</strong></td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Zn</strong></td>
<td>0.5</td>
<td>Causes dizziness and fatigue</td>
<td></td>
</tr>
</tbody>
</table>

Vinceti et al. (2001)

Hess and Schmid (2002)
<table>
<thead>
<tr>
<th>Source</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Hg</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
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<tr>
<td>Agriculture and food waste</td>
<td>0 − 0.06</td>
<td>0 − 0.3</td>
<td>4.5− 90</td>
<td>3-38</td>
<td>0 − 1.5</td>
<td>6− 45</td>
<td>1.5− 27</td>
<td>12 − 150</td>
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<td>Farmyard manure</td>
<td>1 – 4.4</td>
<td>0.2 – 1.2</td>
<td>10− 60</td>
<td>14 − 80</td>
<td>0 − 0.2</td>
<td>3 – 36</td>
<td>3 − 20</td>
<td>15 − 320</td>
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<tr>
<td>Logging and timber</td>
<td>0 − 3.3</td>
<td>0 − 2.2</td>
<td>2.2− 18</td>
<td>3.3− 52</td>
<td>0 − 2.2</td>
<td>2.2− 23</td>
<td>6.6− 8.2</td>
<td>13 − 65</td>
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<td>Municipal waste</td>
<td>0.09 – 0.7</td>
<td>0.88 – 7.5</td>
<td>6.6− 33</td>
<td>13− 40</td>
<td>0 – 0.26</td>
<td>2.2– 10</td>
<td>18– 62</td>
<td>22– 97</td>
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<td>Organic wastes</td>
<td>0 − 0.25</td>
<td>0 − 0.01</td>
<td>0.1– 0.48</td>
<td>0.04– 0.61</td>
<td>–</td>
<td>0.17– 3.2</td>
<td>0.02– 1.6</td>
<td>0.13− 2.1</td>
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<td>Metal processing solid wastes</td>
<td>0.01 – 0.21</td>
<td>0 − 0.08</td>
<td>0.65– 2.4</td>
<td>0.95– 7.6</td>
<td>0 − 0.08</td>
<td>0.84− 2.5</td>
<td>4.1– 11</td>
<td>2.7– 19</td>
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<td>Coal Ash</td>
<td>6.73 – 13</td>
<td>1.5 – 13</td>
<td>149− 446</td>
<td>93– 335</td>
<td>0.37 – 4.8</td>
<td>56– 279</td>
<td>45– 242</td>
<td>112– 484</td>
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<td>Fertilizer</td>
<td>0 − 0.2</td>
<td>0.03– 0.25</td>
<td>0.03– 0.38</td>
<td>0.05– 0.58</td>
<td>–</td>
<td>0.20– 3.5</td>
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<td>Marl</td>
<td>0.04 − 0.5</td>
<td>0 − 0.11</td>
<td>0.04– 0.19</td>
<td>0.15– 2.0</td>
<td>0 – 0.02</td>
<td>0.22– 3.5</td>
<td>0.45– 2.6</td>
<td>0.15– 3.5</td>
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<td>Commodity impurities</td>
<td>36 – 41</td>
<td>0.78– 1.6</td>
<td>305– 610</td>
<td>395– 790</td>
<td>0.55– 0.82</td>
<td>6.5– 32</td>
<td>195– 390</td>
<td>310– 620</td>
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<td>Atmospheric deposition</td>
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<td>2.2 – 8.4</td>
<td>5.1– 38</td>
<td>14– 36</td>
<td>0.63– 4.3</td>
<td>11– 37</td>
<td>202– 263</td>
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<td>Total</td>
<td>52 − 112</td>
<td>5.6 − 38</td>
<td>484− 1309</td>
<td>541– 1367</td>
<td>1.6– 15</td>
<td>106– 544</td>
<td>479– 1113</td>
<td>689– 2054</td>
</tr>
</tbody>
</table>
Table 4. Heavy metal concentrations in polluted soil of selected countries (mg/kg). Modified from (Chao et al. 2014)

<table>
<thead>
<tr>
<th>Country</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Ni</th>
<th>Cd</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing</td>
<td>35.6</td>
<td>23.70</td>
<td>28.60</td>
<td>65.60</td>
<td>27.80</td>
<td>0.15</td>
<td>Zheng et al. (2008)</td>
</tr>
<tr>
<td>Hong Kong</td>
<td>23.10</td>
<td>23.30</td>
<td>94.60</td>
<td>125.00</td>
<td>12.40</td>
<td>0.62</td>
<td>Li et al. (2004)</td>
</tr>
<tr>
<td>Syria</td>
<td>57.00</td>
<td>34.00</td>
<td>17.00</td>
<td>103.00</td>
<td>39.00</td>
<td>-</td>
<td>Moller et al. (2005)</td>
</tr>
<tr>
<td>France</td>
<td>42.08</td>
<td>20.06</td>
<td>43.14</td>
<td>43.14</td>
<td>14.47</td>
<td>0.53</td>
<td>Hernandez et al. (2003)</td>
</tr>
<tr>
<td>Spain</td>
<td>-</td>
<td>57.01</td>
<td>1505.45</td>
<td>596.09</td>
<td>-</td>
<td>3.76</td>
<td>Rodriguez et al. (2009)</td>
</tr>
<tr>
<td>Iran</td>
<td>63.79</td>
<td>60.15</td>
<td>46.59</td>
<td>94.09</td>
<td>37.53</td>
<td>1.53</td>
<td>Sayadi and Rezaei (2014)</td>
</tr>
<tr>
<td>Finland</td>
<td>59.00</td>
<td>23.00</td>
<td>17.00</td>
<td>90.00</td>
<td>24.10</td>
<td>0.17</td>
<td>Salonen and Korkka Niemi (2007)</td>
</tr>
<tr>
<td>Heavy Metal</td>
<td>Maximum Contamination Level (mg/L)</td>
<td>Sources of Contaminant in Drinking Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>-----------------------------------</td>
<td>-----------------------------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>0.010</td>
<td>Erosion of natural deposits, runoffs from orchards and glasses, and electronic production wastes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.005</td>
<td>Corrosion of galvanized pipes, erosion of natural deposits, discharge from metal refineries, runoff from waste batteries and paints</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>1.3</td>
<td>Corrosion of household plumbing systems, erosions of natural deposits</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.015</td>
<td>Corrosion of household plumbing systems, erosions of natural deposits</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>0.002</td>
<td>Erosion of natural deposits, discharge from refineries and factories, runoff from landfills and cropland</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 6. Five main strategies involved in phytoremediation (Pilon 2005)

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phytotransformation</td>
<td>An incomplete or absolute breakdown/degradation of complex organic molecules within plant tissues.</td>
</tr>
<tr>
<td>Phytostimulation</td>
<td>A condition that allows the seepage of plant enzymes or secretion into the root zones to induce or enhance the metabolic activities of relevant microbes for the breakdown of organic pollutants.</td>
</tr>
<tr>
<td>Phytoextraction</td>
<td>A stage that uses pollutant-accumulating plant to eliminate high metal concentration from soil by depositing them in plants parts that can be harvested.</td>
</tr>
<tr>
<td>Phytostabilization</td>
<td>The option that utilizes plants to minimize or restrict the movement of pollutants of interest. This process is achieved by using plants as barriers to erosion, leaching, or other runoffs as a way of mitigating bioavailability of the pollutants within the environment. Thus, pollutant entry into groundwater or food chain is considerably minimized.</td>
</tr>
<tr>
<td>Phytovolatilization</td>
<td>This process is the volatilization of pollutants or metabolites using plants. Most pollutants, especially the volatile organic carbons, are removed via this process. However, some inorganics, such as selenium and mercury, are volatile, and they can be removed with this technology.</td>
</tr>
</tbody>
</table>
Table 7. Cd accumulation in different plant samples (Chen and Lee 1997)

<table>
<thead>
<tr>
<th>Plant species</th>
<th>Concentration of Cd in the leaves (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Celosia argentea</em></td>
<td>86</td>
</tr>
<tr>
<td><em>Pentas lanceolata</em></td>
<td>44</td>
</tr>
<tr>
<td><em>Verbena tenera</em></td>
<td>42</td>
</tr>
<tr>
<td><em>Cosmos bipinnatus</em></td>
<td>13</td>
</tr>
<tr>
<td><em>Salvia splendens</em></td>
<td>12</td>
</tr>
<tr>
<td><em>Zinnia elegans</em></td>
<td>10</td>
</tr>
<tr>
<td><em>Osmanthus spp.</em></td>
<td>4</td>
</tr>
<tr>
<td><em>Rhododendron spp.</em></td>
<td>3</td>
</tr>
</tbody>
</table>
Table 8. Examples of contaminant-accumulating plants (Alberto and Sigua 2012)

<table>
<thead>
<tr>
<th>SCIENTIFIC NAME</th>
<th>COMMON NAME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Armeria maritima</td>
<td>Seapink thrift</td>
</tr>
<tr>
<td>Ambrosia artemisiifolia</td>
<td>Ragweed</td>
</tr>
<tr>
<td>Brassica juncea</td>
<td>Indian mustard</td>
</tr>
<tr>
<td>Brassica napus</td>
<td>Rape, rutabaga, turnip</td>
</tr>
<tr>
<td>Brassica oleracea</td>
<td>Flowering/ornamental kale and cabbage, broccoli</td>
</tr>
<tr>
<td>Festuca ovina</td>
<td>Blue/sheep fescue</td>
</tr>
<tr>
<td>Helianthus annuus</td>
<td>Sunflower</td>
</tr>
<tr>
<td>Thalspi rotundifolium</td>
<td>Pennycress</td>
</tr>
<tr>
<td>Triticum aestivum</td>
<td>Wheat (scout)</td>
</tr>
<tr>
<td>Zea mays</td>
<td>Corn</td>
</tr>
</tbody>
</table>