Abioye O Fayiga* and OC Nwoke

College of Agriculture, Osun State University, Osogbo, Osun State, Nigeria

Review Article

Metal (Loid)s in Farmland Soils and Strategies to Reduce Bioavailability

Abstract

High concentrations of heavy metal (loid)s (HMs) in farmland soils reduces crop yield and contaminates the food chain. Exposure to HMs in the diet results in several adverse health effects such as cancer, reproductive health problems and cardiovascular diseases. Understanding the origin and fractionation of these toxic substances will provide direction for reducing their bioavailability in contaminated farmland soils. HMs are added to farmland soils through activities such as irrigation, organic and inorganic fertilization, pest control, and mining. Weathering of parent material and atmospheric deposition can also increase the levels of HMs in the soil. Fractionation of HM contaminated soils provides information on availability of HMs such as Pb, Cd, As, Cr and Cu to soil biota and plants. Several studies have reported that Pb is mostly associated with Fe and manganese oxides (reducible fraction) while Cd is mostly associated with the most mobile fraction (exchangeable fraction). The application of organic and inorganic soil amendments such as vermiculite, zeolite, composts and crop residue to contaminated farmland soils converts HMs from the plant available fractions to the less mobile fractions. HM resistant microbes can change HMs to a less mobile fraction or less mobile oxidation state. The combination of HM resistant microbes, HM tolerant plants, and soil amendments can be used to reduce mobility of HMs in contaminated farmlands.

Capsule: The mobility of heavy metal (loid)s in polluted farmland soils depends strongly on its association with soil components.

Introduction

Total soil concentrations of heavy metal (loid)s (HMs) are increasing in agricultural soils globally due to both natural and anthropogenic sources in the environment. Several studies have reported HM concentrations above acceptable limits in farmland soils [1–4]. However, total soil concentrations do not provide enough information about the availability or toxicity of HMs to soil biota and growing plants.

HMs can be bound to solid constituents of the soil such as clay, organic matter, carbonates, sulfides, iron (Fe) and manganese (Mn) oxides, which reduces its availability for plant uptake. The amount of HM available to soil biota and plants is referred to as bioavailability. Bioavailability is a better estimate of the environmental impact of contaminated soils. The bioavailability of HMs depends strongly on the sources of contamination, speciation and fractionation of HMs in the soil.

Plant uptake of HMs in contaminated soils is dependent on the fractionation and mobility of HMs in the soil. However, depending on tolerance levels, plant species may either exclude or accumulate toxic HMs from contaminated soils. Food crops growing on HM contaminated soils show a reduction in growth, performance, and yield [5]. Several studies have reported a decline in crop yield and quality in metal polluted farmland soils [6–8]. Declining crop yield due to metal pollution of agricultural soils is a threat to global food security.

HM contamination of farmland soils may also contaminate the food chain and cause health problems in nearby communities [9]. HM contamination of farmland soils has led to high concentrations of HM in food crops such as rice grains, wheat and vegetables [10–12]. These food crops are staples in many countries worldwide indicating that food chain contamination exposes a large population of consumers to the adverse effects of HMs.

HMs disrupts metabolic activities which affects virtually every organ and system in the body. Exposure to arsenic (As) has been associated with health problems such as cancer, cardiovascular and respiratory diseases, hearing impairment, reproductive health problems in pregnant women and it affects the unborn [13]. Lead (Pb) is especially dangerous to infants and young children because it can damage their developing brain while adults can suffer from reproductive

009

health problems, high blood pressure, digestive problems, neurological disorders, memory and concentration problems, muscle and joint pain, and kidney dysfunction [14]. Cadmium (Cd) is toxic to the kidney while chromium (Cr) exposure can lead to problems in the respiratory system, gastrointestinal system and skin [15,16].

It is important to reduce the bioavailability of HMs in contaminated agricultural soils in order to prevent the health hazards of HM and reduce economic losses to farmers due to reduction in crop yield. Sustaining high crop yields is very important to ensure adequate food supply for the increasing population in the world. There are a variety of strategies and techniques that can be used to control and reduce mobility and bioavailability of HMs in farmland soils.

While some strategies can be used to remove contaminants permanently, some others can only be used to reduce the migration of contaminants in the soil. Physical methods that severely alter soil structure such as capping of soil with cement are not suitable for farmland soils. The selection of the right technique will depend on site characteristics, operation costs, source of contamination and contaminant chemistry.

In order to effectively remove, control and reduce mobility of HMs in contaminated soils, it is imperative to identify the sources of contamination, understand fractionation of HMs and the factors that enhance their mobility in contaminated soils. Hence this paper provides a review of sources of contamination, fractionation and mobility of HMs in farmland soils as well as strategies for reducing their bioavailability.

Heavy metal (loid)s in farmland soils

Sources

Anthropogenic sources: Anthropogenic sources (Figure 1) of HMs include agricultural activities and industrial activities which contribute to elevated concentrations of HMs in the environment [17]. Sources depend on location, farm management practices and environmental conditions. Major sources of HMs reported for England and Wales include industrial activities, sewage sludge, animal manures and composts, inorganic fertilizers and lime, agrochemicals, and irrigation water [18].

The quality of water used for irrigation is important because it has been associated with metal pollution in farmland soils.

Sewage irrigated soil contained much higher concentrations of Cd, copper (Cu), Pb, zinc (Zn), nickel (Ni), Cr, as and mercury (Hg) compared to clean water irrigated soil [19]. Scarcity of high quality water sources for irrigation has forced many farmers to use industrial wastewater or sewage water/sludge with high metal concentrations. Consequently, farmlands irrigated with industrial wastewater for 30 years became heavily polluted with HMs [2].

Wastewater irrigation of vegetable gardens in Zimbabwe also increased concentrations of HMs in the soil [1]. The use of wastewater also contaminates the crops growing on the irrigated farmland soils. Green vegetables irrigated with wastewater had higher concentrations of HMs than vegetables irrigated with well water in Pakistan [20]. However, in regions with arsenic contaminated groundwater, the use of well water for crop irrigation has also led to soil and crop contamination [10,12, 21].

Surface waters are also another source of irrigation water in farmlands. However, these surface water sources may be polluted due to discharge of urban and industrial waste into rivers. Irrigation of alfalfa fields with river water has been reported to account for up to 31 % of HMs in surface soils of Texas and Mexico [22]. Long term irrigation with river water polluted by mining operations in Jiangxi Province of China resulted in heavy metal (loid)s pollution of the soil with the concentrations of the two primary pollutants in the soils varying from 0.52–2.55 mg kg^{-1} for Cd and 27.87–426.15 mg kg^{-1} for Cu [23]. Higher concentrations of HMs were found in the agricultural soils closer to mines and metal smelters than in other soils.

The mining of HMs often lead to contamination of nearby agricultural soils [24]. For example, mining activities in Tunisia has led to high concentrations of Pb (17,229 mg kg^{-1}), Zn (4813 mg kg^{-1}) and Cd (42 mg kg^{-1}) in nearby agricultural soils [3]. Elevated concentrations of HMs were also reported in wheat grown in these contaminated soils. Pb concentrations were 1824 and 54 mg kg^{-1} and Zn concentrations were 1546 and 636 mg kg^{-1} in the roots and shoot respectively. These concentrations are far above acceptable limits and indicate potential health risks for consumers.

Even when concentrations of HMs in irrigation water were below permissible limits, high levels of HMs were found in vegetable cultivated in farmlands of Northern Ethiopia [25].
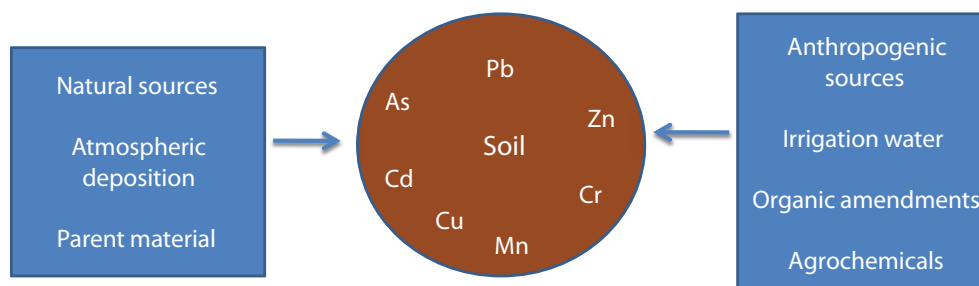

Figure 1: Sources of contamination in farmland soils.

This suggests that the established acceptable limits were not effective to prevent contamination of the food chain. Similarly, the use of treated sewage water in Saudi Arabia led to an increase in HM levels in soils and test crop (okra) [4]. This suggests that pretreatment of sewage water was not able to remove a large portion of heavy metals contained therein.

The use of organic manures such as biogas slurry in vegetable farmlands of the Taihu Basin, China led to high concentrations of Ni, Zn, Cd and Pb in vegetables and soils above acceptable limits [11]. Livestock manures and sewage sludge were found to be responsible for 37–40 and 8–17% of total Zn and Cu inputs, respectively, in farmland soils of England and Wales [17].

Long term use of agrochemicals such as fertilizers and pesticides (insecticides, herbicides and fungicides) to increase crop yield often contribute to HM pollution because of their composition and soil characteristics. In a past study, the high concentrations of As, Pb, and Cd in agricultural soils were attributed to the application of agrochemicals [26]. A previous study has also shown that copper based fungicides have the potential to increase concentration of Cu in the soil to phytotoxic levels [27]. P fertilizer treatments increased the Zn solution concentration in 83% and 53% of treatments while it increased the concentration of Cd by 87% and 80% in field and laboratory experiments respectively [28]. Agricultural activities that may increase HM concentration in the soil include use of contaminated irrigation water, mostly from industrial or domestic wastewater, sewage sludge or bio solids; use of farmyard manure with high HM concentration; use of agrochemicals such as fertilizers and pesticides.

Natural sources: Natural sources of heavy metal (loid)s (HMs) include parent material and atmospheric deposition from volcanic activity and forest fires. Soils are formed as a result of a long period of physical and chemical weathering of the underlying parent rock. Physical weathering breaks the soil into smaller sizes while chemical weathering releases minerals present in the parent rocks which forms part of the soil. These minerals are sources of essential plant nutrients and heavy metal (loid)s.

Parent material was associated with the high concentrations of Cu, Cr, Ni, Pb and As of farmland soils of the urban-rural transition zone in [29]. The soil parent material and point sources of pollution significantly contributed to Cr, Ni, Cu, Zn and Cd levels in agricultural soils [30]. The extent of contamination has been found to depend greatly on the mobility of the metal (loid)s.

It has been estimated that atmospheric deposition was responsible for about 25–85% of total inputs of HMs in agricultural soils in England and Wales [18]. HM contamination in topsoil from remote farmland in China was attributed to long range transport and atmospheric deposition of HMs since no pesticides or fertilizers have been used in the remote farmland stations studied and no industries were situated nearby [31].

Sometimes, human activities such as urbanization, industrialization and mining also contribute to atmospheric deposition. Increased levels of metals in the soil have been attributed partly to atmospheric fallout from a local ore smelter in alfalfa fields in Texas and Mexico. Metal concentrations in unwashed alfalfa forage tissue were at least five times less than those in soil and showed no consistent association with soil concentrations [22].

Industries are responsible for atmospheric deposition of mercury (Hg) in agricultural soils of a rapidly industrializing area [30]. Ferroalloy industries in Brescia province, Italy produced particulate emissions enriched in Mn, Pb, Zn, Cu, Cd, Cr, Fe, and aluminum (Al). This was responsible for the HM (Al, Cd, Fe, Mn, Pb, and Zn) contamination of home gardens close to the industries. Unwashed spinach showed higher metal concentrations than washed spinach indicating atmospheric deposition [32].

Sometimes, the presence of HMs in the soil may be due to multiple sources. The results of a multivariate geostatistical method showed that Cd, Cr, and Cu in reclaimed farmland soils was associated with chemical fertilizers, Pb and Zn with atmospheric deposition and Ni was associated with the electroplating factories' wastewater discharge [33]. Atmospheric deposition of Pb and Zn may be from vehicular emissions from nearby roads and highways and industrial emissions.

In a representative agricultural suburb in Beijing, China, multivariate and geostatistical analyses indicated that soil contamination of Cd, Cu and Zn was mainly derived from agricultural practices. As and Pb were due mainly to soil parent materials, while Hg was caused by the atmospheric deposition of particulate matter [34]. In Taiyuan City, China, HMs (Cd, Cu, Hg, Pb, Zn, and Cr) contamination of agricultural soils was attributed to farming practices while as and Ni were associated with parent material [35]. Contamination of soils with as is commonly associated with parent material because it can be mobilized naturally through evaporative concentration, leaching from sulfides by carbonate, and microbial mobilization [36].

Bioavailability of heavy metal(loid)s in farmland soils

Bioavailability provides information on the amount of contaminants available for chemical reactions or plant uptake. Total HM concentrations are insufficient to determine its environmental impact in contaminated soils because HMs are often bound by different soil constituents such as organic matter, Fe/Mn oxides and clay minerals [37]. Sequential extractions with different extractants are often used to partition metals into operationally defined chemical associations in the soil.

Though there are several methods of sequential extractions for HMs, the most common one is the five stage extraction method (Figure 2) which separates HMs into five different fractions; water soluble and exchangeable fraction; bound to carbonate; bound to iron and manganese oxides (reducible oxides/oxidic fraction); bound to organic compounds and sulfides; and residual fraction [38].
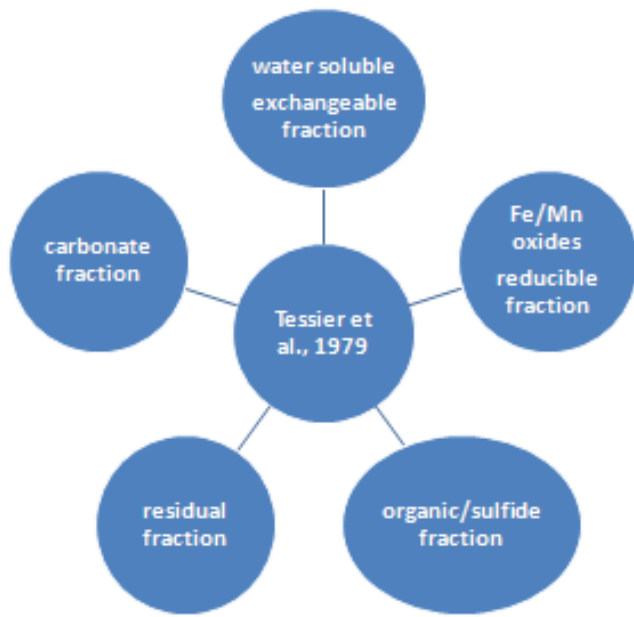
Figure 2: Fractionation of heavy metal (loid)s in the soil.

Another method was developed by the European Community Bureau of Reference, called the BCR method [39,40]. The BCR method is a three step procedure that extracts the exchangeable and carbonate-bound fractions in a single step versus the two steps used in the Tessier procedure [41]. The fractions extracted by the BCR method are; exchangeable (extraction step 1), reducible-iron/manganese oxides (extraction step 2), oxidizable-organic matter and sulfides (extraction step 3) [42].

The fractionation method for metals may not be appropriate for metalloids such as vanadium (V), as, and Se. The method for phosphorus (P) fractionation is used for As contaminated soils because of similarities between us and P. Sequential extraction of As is a four step procedure separating into four fractions; water-soluble and exchangeable fraction, Al-bound fraction, Fe-bound fraction and the Ca-bound fraction [43].

Fractionation of heavy metal (loid)s in Agricultural soils; Fractionation of HMs into operationally defined fractions is important because it shows the distribution between different soil components and provides information on potential mobility of HMs in the soil. Fractionation of HMs in farmland soils depends on the soil properties, sources, cropping systems, farm management practices and plant species.

Pb was mainly associated with the reducible fraction (bound to Fe and Mn oxides) while Cu, Zn and Cd were dominated by the residual fraction in agricultural and nonagricultural soils [44]. Similarly, V and Pb were associated with the reducible fraction, Hg and Cd with the exchangeable fraction, Co with the carbonate fraction, while Cr, Cu, Zn, Ni were mostly associated with the oxidizable fraction in agricultural soils contaminated by wastewater irrigation in Ethiopia. There was a higher concentration of HMs in the non-residual fractions than the residual fraction suggesting high mobility of HMs in the soil [45].

Some other studies have also shown that Pb was strongly associated with the reducible fraction. Fractionation of agricultural soils close to mines and smelters showed that Pb was in the reducible fraction; Cd in the exchangeable and carbonate fraction while Cu and Zn were mainly in the residual fraction [23]. The reducible fraction was the largest fraction for Cu and Pb in agricultural soils contaminated from improper disposal of tailings [24].

On the contrary, Pb and Cu seemed to be more tightly bound to the organic fraction while cadmium was mostly bound to the Fe/Mn oxides fraction in contaminated soils from Sicily; though a significant amount of all HMs (Cd, Pb, Cu, Co, Cr, Fe, Mn, Ni, Zn) were bound to the organic fraction [46]. The oxidic fraction usually has more affinity for Pb than Cd, so this may be due to high concentration and strong negative charges on organic fraction of the soil.

The partitioning of agricultural soils contaminated with wastewater or smelter dust demonstrates how organic matter content may influence fractionation of HMs. HMs in the wastewater polluted soil (with high organic matter) were mostly bound to the organic fraction in the wastewater while they were mainly associated with Fe/Mn oxides in the smelter dust polluted soil. Cadmium was mostly in the exchangeable fraction in both soils while lead in the smelter dust polluted soil was dominated by the reducible fraction [47].

Cd in soil profiles was predominantly associated with the exchangeable fraction while Pb was closely associated with reducible fraction in a BCR extraction of contaminated vegetable soils from the Pb/Zn mining and smelting areas of China [48]. The mobile fractions (exchangeable, reducible, and oxidisable) of Mn, Cd and Pb were higher than the immobile fractions (residual) in a modified BCR extraction of contaminated agricultural fields of Çanakkale, Turkey [49].

There was also a strong correlation between concentrations of HMs in corn grain and the more available fractions (exchangeable and reducible) [49]. Cu Cr, Ni and Zn were mostly in the residual fraction; Cd was mainly associated with the exchangeable/carbonate and reducible fractions, while Pb was mainly associated with the reducible fraction in a BCR extraction of compost amended and unamended field plots [50].

Several studies have reported that Pb is mostly associated with the reducible fraction (bound to Fe/Mn oxides) while Cd is mostly associated with the most mobile fraction (exchangeable fraction) [24,44,45,48]. This may be due to higher affinity of oxidic surfaces in the soil for Pb than for Cd. This may explain why Cd had the highest transfer factor in vegetables grown in farmlands amended with biogas slurry [11]. Cd was probably very mobile in the amendment and treated soil.

Guillén et al. [17], reported that Cd poses a serious threat to human health and the environment due to the high percentage of mobility. The high mobility of Cd might be responsible for the high accumulation of Cd in wheat grains reported in China [51]. Additionally, a study on metal accumulation in farmland

soils across China reported that Cd had the highest pollution index [52]. Furthermore, Cd has been reported as a major contaminant in rice fields of East and South Asian countries [53]. All these suggest that Cd is a threat to food security in Asian countries due to its high mobility.

It has been shown that metals with anthropogenic sources were mainly associated with residual, oxidizable and reducible phases which are relatively immobile and only potentially bioavailable to plants. However, micronutrients such as Zn and Cu showed a tendency to become more readily mobile and bioavailable as their total content in soil increased and were more easily transported to the edible parts of lettuce than other pollutants [54].

Fractionation of HMs in contaminated agricultural soils also varies with soil classification. A greenhouse experiment with rice grown in two paddy soils showed that Pb was more mobile in the Ultisol (Plinthudic Aqults) than in the Inceptisol (Fluventic Umbrepts) because Pb in Ultisol was mostly associated with the residual and exchangeable fractions, while Pb was mainly associated with the residual and Fe/Mn oxides fractions in the Inceptisol [55]. This suggests that Pb will be more available to plants in the inceptisol while it will be less available in the ultisol.

Phytoavailability of heavy metal (loid)s in agricultural soils: Phytoavailability is a measure of the amount of HMs available in the soil solution for plant uptake. Phytoavailability of trace elements especially HMs depends on their speciation rather than on total soil concentrations [56]. Speciation of HMs determines their fractionation in the soil and availability for plant uptake. Phytoavailability of HMs can be measured either by single extractions or directly by plant uptake in contaminated soils.

Four single extractants commonly used include; calcium chloride ($CaCl_2$), diethylene triamine pentaacetic acid (DTPA), ethanoic acid (CH_3COOH), and water [57]. Some other single extractants include Mehlich 3, ammonium nitrate (NH_4NO_3), sodium nitrate ($NaNO_3$), ethylene diamine tetraacetic acid (EDTA) and nitric acid (HNO_3) [58].

Some studies have reported significant correlation between concentrations of HMs in single extractants and plant uptake [57-60]. Lavado et al. [59], reported significant correlations between EDTA extractable copper in soils and maize grown in biosolids amended soils. Wang et al. [57], also reported that the phytoavailability of HMs to Chinese cabbage was significantly correlated with concentrations of metal extracted by $CaCl_2$. However, phytoavailability was influenced by soil properties such as soil pH, organic matter and cation exchange capacity (CEC).

Fractions of HMs in sequential extractions have also been correlated with plant uptake. The Cr concentration of rice grain had the highest correlation with water soluble and exchangeable Cr while the straw Cr best correlated with the Fe and Mn oxide fraction [61]. The sum of the metal percentages extracted from the first two fractions of Tessier's procedure

was found to be suitable in predicting the phytoavailability (to *Lactuca sativa* and *Spinacia oleracea*) of most of the HMs present in the soil of a contaminated site in Piedmont, Italy [62].

On the contrary, NH_4NO_3 extractant was ineffective in determining the availability of HMs (Cd, Cr, Cu, Ni, Pb and Zn) for sugarcane [63]. Even though DTPA extraction indicated higher metal availability in sludge amended soils, it did not increase HM concentration in plant leaves, suggesting that determination of HM availability by extraction may not accurately predict phytoavailability [64].

A series of empirical equations involving extractable metals, solid-phase fractions and soil properties have been used to significantly predict the phytoavailability of Mn and Zn for barley [65]. The importance of solid-phase Cd fractions, EDTA fraction and/or HNO_3 fraction, in predicting phytoavailability of Cd in soils amended with manure compost have also been demonstrated [66].

Leafy vegetable *Amaranthus hybridus* had 1.2–8.2 folds enrichment of Cr, Co, Ni, Cd, Cu, and Pb than *Abelmoschus esculentus* in amended soils irrigated with wastewater suggesting that phyto-accumulation of HMs is plant-specific and dependent on physiological set-up [67]. Metal accumulation in vegetables grown in urban gardens varied by crop type further confirming that phytoavailability may vary with crop type [68].

This may explain why phytoavailability of Cd to rice grain was strongly correlated with Mehlich-3-extractable Cd while the same Mehlich-3 extractant was not efficient to evaluate Ni phytoavailability to maize plants [69,70]. This suggests that soil extractions may not be the best method to determine phytoavailability of Cd. It has been shown that the soil type, Cd source, loading rate, soil pH, and plant tissue are important factors in evaluation of Cd phytoavailability [66,70].

Factors influencing the mobility of heavy metal(loid)s in agricultural soils

Soil properties: Soil properties such as pH, soil texture, organic matter content, Fe/Al oxides and moisture content control metal mobility (Figure 3) in soils [71]. Amongst all, pH is a major factor controlling the mobility of HMs in contaminated soils. Soils with low pH have higher concentrations of HMs in the most mobile/soluble phase (exchangeable fraction) [72]. HM concentrations significantly increased while pH decreased down the soil profile to a depth of 30cm [73]. HMs are more available at a low pH probably because there is a higher concentration of protons displacing the metals from exchange sites on the solid phase of the soil.

Recently, it was shown that increasing the soil pH to 10 can decrease the zinc content of *Valeriana officinalis* significantly [74]. Decrease in heavy metal mobility with increasing soil pH has been attributed to precipitation of hydroxides, carbonates or formation of insoluble organic complexes [75]. On the contrary, increasing pH increased Cu and Mn in plant tissue of *V. officinalis* probably due to formation of soluble organo-metal complexes at high pH [74].
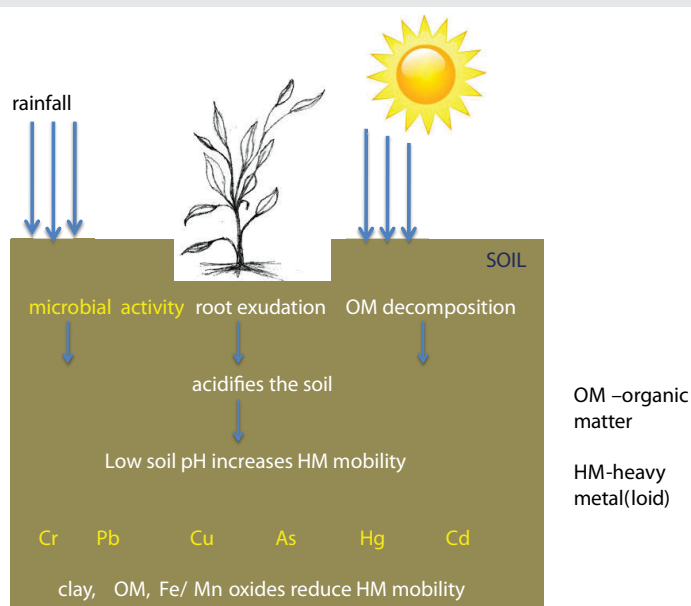
013

Figure 3: Factors enhancing mobility of metal (loid)s in farmland soils.

A past study showed that Zn concentrations in the soil increased with increasing soil acidity while it decreased with increasing clay content of the soil [76]. This indicates that soil texture also plays an important role in metal mobility and retention in the soil. Generally, there is a higher mobility of HMs in sandy soils than clayey soils [77]. Adsorption of the HMs on clay surfaces retards the movement of HMs and reduces leaching and run off.

Soil organic matter (SOM) is also an important adsorbent for HMs in agricultural soils because of the presence of charges which reduces their mobility and availability in the soil. The presence of SOM decreased Zn binding energy, increased immobilization of Zn and decreased the proportion of nonspecific adsorbed Zn [78]. Metal release due to solubilisation of organic matter and formation of organo metallic complexes has also been reported in agricultural soils [79,80].

Fe and Mn-oxides and hydroxides also play an important role in heavy metal sorption due to their high specific surface area and reactivity [81]. The strong affinity between oxidic surfaces (of Fe, Al and Mn) in the soil and HMs makes them effective adsorbents of HMs. Hence, increasing concentrations of Fe/Al/Mn oxides in the soil reduces the mobility and phytoavailability of HMs in the soil [77].

The mobility of HMs is determined by their concentration in the soil solution which depends on amount of soil moisture. It was found that soil moisture regime significantly affected the transformation rate from the more mobile fractions (exchangeable) to the less labile ones (Fe-Mn oxide and organic matter-bound fractions). In general, the paddy soil under flooding regime had higher metal reactivity compared with 75% field capacity and wetting-drying cycle regimes, resulting in the more complete movement of metals toward stable fractions [82].

It is well known that metal availability decreases as the soil

ages [83-87]. During aging, as moved from the more available (non-specifically and specifically sorbed) to less available (amorphous and crystallized Fe/Al) fractions while Pb moved from the first three fractions (exchangeable, carbonate and Fe/Mn hydroxide) to organic fraction [88]).

Environmental conditions: Environmental conditions such as rainfall, temperature and wind greatly impact the fate and transport of metals [89]. Rainfall events increase soil and water runoff which also increases the mobility of HMs in agricultural soils [90]. Less than 4% of Cu and more than 58.3% of Zn were transferred from composts to groundwater under simulated rainfall conditions in a soil column experiment [91]. This suggests that the effect of rainfall may depend on the chemistry of HM being investigated and their interaction with the soil. Rainfall can also increase the area impacted by metal contamination by increasing the distance travelled by HMs applied in composts, sewage sludge, farmyard manure and bio solids.

Chemical composition of rainwater is responsible for its effect on the mobility of HMs. It is well known that gaseous air is a mixture of gases such as oxygen, nitrogen, carbon dioxide and sulfur dioxide. Normal rain is slightly acidic because the carbon dioxide in the air dissolves in rainwater to form carbonic acid, a weak acid. Acid rain occurs when there are high concentrations of sulfur dioxide and nitrogen oxides in the air. Dissolution of sulfur dioxide in rainwater may produce sulfuric acid while nitrogen oxides may form nitric acid. These are both strong acids and their presence in rainwater acidifies the soil.

Acid rain lowers the soil pH and increase metal mobility in the soil [92]. Acid rain is caused by volcanic activity, fossil fuel emissions, wildfires and lightning and has been reported in several countries including USA and South Korea [93]. This acidic input may further exacerbate metal pollution and cause leaching in agricultural soils. A study on the effect of simulated acid rain on metal mobility found that Cu and Zn were released by the soil in larger amounts than Pb and Cd [94].

Temperature is also another environmental condition that may impact metal mobility. High temperature will increase rate of organic matter decomposition (Figure 3) which may lead to formation of organic acids that acidifies the soil and increase metal dissolution and mobility. High temperature may also lead to higher microbial activity which may either decrease or increase metal mobility. A past study has shown that microbes reduced as and metal concentrations in the absence of organic matter but increased metal concentrations in the presence of organic matter [95].

Higher microbial activity may lead to lower metal mobility due to microbial reduction of metals to a lower redox state that is less mobile [96]. Bacteria reduced metal mobility (reduced water-soluble Pb) due to adsorption by bacterial cell walls and possible sedimentation reactions with phosphate or other anions produced through bacterial metabolism [97]. Metal mobilization by soil microorganisms can arise from complication and methylation while immobilization can result from sorption to biomass or exopolymers, transport

and intracellular sequestration or precipitation as organic and inorganic compounds [98].

Plant characteristics: The presence of plants in the soil can increase metal mobility by increasing acidity via processes like root exudation, acidifying effects of CO_2 produced in root respiration and H^+ released due to cationic nutrient intake [99]. Plant roots produce low molecular weight organic acids (LMWOA) which have the potential to enhance metal mobility in the soil by reducing soil pH and forming complexes with HMs [100].

On the other hand, some studies have reported that root exudates reduced metal mobility due to their strong metal binding ability [101,102]. The immobilization of metals by root exudates may be a coping mechanism for exclusion (reduced uptake) of toxic HMs in nonmetal hyperaccumulators [103,104]. Metals present in the rhizosphere of hyperaccumulators are more bioavailable than those in the rhizosphere of non hyperaccumulators [105-107]. However, root exudates produced by the Cd and Zn hyperaccumulator *Thlaspi caerulescens* did not significantly increase metal mobility [101,108].

Root exudates are an abundant source of energy and nutrients for microorganisms which exists in associations with plant roots in the soil [109]. Plants usually form symbiotic associations with microorganisms such as rhizobacteria and arbuscular mycorrhizal (AM) fungi. AM fungi in symbiotic associations with a range of plant species are able to enhance uptake of nutrient elements and water by host plants through their extraradical mycelial networks [6].

Some of these microorganisms are able to tolerate high concentrations of HMs and have evolved resistance strategies [110]. Arsenic resistant bacteria have been isolated in the rhizosphere and plant tissues of an as hyper accumulator [111,112]. Arsenic resistant rhizobacteria and AM fungi have been shown to increase as uptake and translocation in the as hyperaccumulator *Pteris vittata* [113-115]. Similarly, a heavy metal resistant bacteria strain, isolated from the rhizosphere of *Elsholtzia splendens* increased the uptake and translocation of copper (Cu) in *E. splendens* [116].

The presence of a bacterium and fungus in agricultural soil increased plant biomass and HM uptake in corn (*Zea mays*) [117]. However, it is also possible for AM fungi and rhizobacteria to decrease metal uptake of the host plant and protect them against heavy metal toxicity. Copper resistant bacteria increased root and shoot length, plant dry weight and leaf area, reduced plant uptake and protected lentil plants from copper toxicity. The plant growth promoting bacteria was also able to improve anti-oxidative defense mechanism of the plants by increasing activities of anti-oxidant enzymes such as catalase and superoxide dismutase [118].

Farm management practices: Management practices such as cropping systems, land management, tillage methods, fertilization and water management influence HM mobility in agricultural soils. A study has shown that cultivation can decrease the humified carbon content and metals bound to

the humic acid fraction of organic matter suggesting that cultivation may potentially increase the mobility of heavy metals [119]. Cropping systems (Table 1) such as crop-legume rotation cropping, continuous alfalfa cropping and application of manure, have been shown to increase Mn availability in rainfed farmland soils [120].

A study investigated the metal contents in open field cultured soils versus soils cultured under shelters. Results showed that the respective average concentrations of Al, Fe and Pb in the soils were 2.66, 1.41 and 2.46 times higher in open fields than soils under shelters, whereas the respective average soil concentrations of Cu and Zn were 1.48 and 1.41 times lower [121]. This was attributed to exposure of open fields to soil erosion from runoff and leaching of Cu and Zn within soil profile [121].

Change in land use or conversions also affect metal mobility. The conversion of farmland from wetland resulted in an increase in the concentration of Pb and Cr in the soil while the concentrations of Zn, Cu, Ni, and Cd decreased when wetland was converted into farmland. The levels of Pb increased by approximately 28.6 % when dry land was converted to wetland and by 24.7 % when paddy land was converted [122].

Land application of organic manure may lead to HM contamination of the soil at the surface layer. Tillage practices in farmland soils may affect mobility of HMs by redistributing HMs. In a previous study, no-tillage simulations showed consistent HM accumulations in the surface soil. Even though soil tillage reduced HM concentrations over the top 20 cm of the soil profile, it increased their transfer to deeper layers [123].

The effect of tillage methods, crop rotation and fertilization on Cd availability in tuber and cereal grains was determined in a study in Europe. Results show a higher plant uptake of Cd in wheat grain in continuous wheat under direct drilling than under reduced till or conventional cultivation [124]. Cd concentration in grain was highest in wheat grown after a legume and lowest in wheat grown after a cereal. Cd in wheat grain and potato tubers can increase with increasing rates of nitrogen regardless of the crop rotation [124].

Table 1: Effect of cropping systems and tillage practices on mobility of heavy metal (loid)s.

Cropping systems	Results	References
Crop-legume rotation	Increased Mn availability	Wang et al., 2016 [125]
Continuous alfalfa	Increased Mn availability	Wang et al., 2016[125]
Wheat-cereal cropping	Low Cd in grains	Mench, 1998 [124]
Wheat-legume cropping	High Cd in grains	Mench, 1998 [124]
Tillage methods		
No tillage	Consistent HM accumulation in top soil	Mallmann et al., 2014 [123]
Tillage	Reduced HM in top soil but increased their transfer to deeper layers	Mallmann et al., 2014 [123]
Continuous wheat under direct drilling	Higher plant uptake of Cd	Mench, 1998 [124]
Continuous wheat under reduced tillage	Lower plant uptake of Cd	Mench, 1998 [124]

A recent study has reported that fertilization generally increased more available fractions (exchangeable and carbonate-bound Mn) in the soil [125]. Similarly, mineral fertilizers increased the mobility of Ni and Cu in a study in Poland [126]. Long-term fertilizer use has been reported to increase soil metal content, soil organic carbon, cation exchange capacity, and decrease soil pH [127]. The acidification of the soil by inorganic fertilizers may be responsible for the increase in metal mobility.

Strategies for reducing bioavailability of metal(loid)s in contaminated farmlands

Stabilization: This method involves the use of soil amendments to limit contaminant migration in contaminated soils. Highly solid materials like cement that changes soil structure cannot be used on farmlands. Organic amendments such as crop residues, farmyard manure, composts, and biochar have been used to reduce mobility of HMs in agricultural soils. Similarly, inorganic amendments such as lime, vermiculite and phosphates have been used to immobilize HMs in contaminated farmland soils.

The incorporation of crop residue into the soil may be an economical method of reducing metal mobility because they are readily available on the farm (Table 2). It also takes care of waste disposal on the farm. The addition of rapeseed residue decreased the mobile fraction of Cd by 5–14% and Pb by 30–39% through their transformation into less available fractions, and reduced metal availability to rice plant in a contaminated paddy soil [128].

Addition of rice straw ash (RSA) to rice paddy soils has been shown to retard the movement of Cu by suppressing the release of Cu into the soil solution and transforming Cu into less soluble forms [129]. Rice straw (69.5% reduction) was more effective at reducing Cd uptake in shoots of maize compared with biochar (50.9% reduction) and wheat straw (66.9% reduction) [130].

Table 2: Techniques for reducing bioavailability of heavy metal (loid)s in farmland soils.

Method	Advantages	Limitations	References
Organic amendments	Readily available Sustainable Increases soil organic matter	May increase pollution	Xu et al., 2016 [130]
Inorganic amendments	Faster immobilization process	High cost of operation	Zhou et al., 2014 [145]
Crop-hyperaccumulating plant rotation	Cheap Environmentally friendly Sustainable	Disposal of HM rich hyperaccumulating plants	Ye et al., 2011 [162]
HM resistant microbes	Limits contaminant migration Relatively cheap	Not suitable for highly contaminated soils.	Li et al., 2016 [147]
Soil washing	Removes contaminant permanently	May reduce soil fertility and microbial activity.	Yi and Sung, 2015 [181]

Biochar, produced from carbonization of organic wastes, has been shown to reduce exchangeable fractions of metals in the soil and decrease plant uptake of HMs in crops such as maize, rice and lettuce [131-133]. Even though biochar has demonstrated potentials of reducing metal mobility in contaminated soils, identifying heavy metal contamination in biochar is crucial before it is used as a soil amendment [134]. Addition of metal rich biochar to lightly contaminated soils may increase metal accumulation in the soil [134].

Even though organic manure may also be a source of HMs, farmyard manure (36-45% reduction) was more efficient than rice husk (23% reduction) and straw dust (14% reduction) in reducing phytoavailability of Cd to *Amaranthus caudatus* [135]. Past study has also shown that increasing rates of Cd applied through chicken or pig manure compost increased its precipitated and residual fractions [66].

Farmyard manure such as pig slurry has been shown to reduce the mobility of Cu in contaminated soils [136]. Although, the application of cow manure and compost to a calcareous contaminated soil increased the solubility of Cu in an incubation experiment, it reduced the mobility of Zn and Pb in the same soil [137]. This suggests that factors such as type of organic amendment, soil type and metal chemistry may affect metal mobility.

Addition of municipal solid waste and manure composts to soil reduced bioavailability and plant translocation of Cu and Zn [138]. It has also been shown that animal manure compost had lower Cd plant uptake (spinach) than soils treated with chemical fertilizers [139]. Furthermore, the addition of 2.5% (dry w/w) municipal compost reduced the Cd concentration in onions, spinach and lettuce by up to 60% in garden soils [140].

Use of fly ash to stabilize sewage sludge has been shown to reduce metal availability to corn by converting metals to less available fractions in the soil [141]. Decontaminated sludge has also been used to reduce bioaccumulation of metals in maize cultivated farmland soils [142]. However, lime was more effective in reducing metal extractability than sewage sludge mixed with green waste compost [143].

A combined application of limestone and red mud reduced $Ca(NO_3)_2$ extractable As, Cd, Pb, and Zn by 58%, 98%, 98%, and 99%, respectively which led to reduction in plant uptake along with an increase in microbial activity [144]. Combined soil amendments limestone+sepiolite and hydroxyhistidine+zeolite reduced exchangeable fraction of metals (Pb, Cd, Cu, and Zn) and inhibited uptake and accumulation of Pb, Cd, Cu, and Zn in rice plants [145]. Inorganic amendments such as vermiculite have also been shown to reduce plant uptake of HMs from contaminated soils [62].

Lime based materials increase pH which reduces metal mobility while other inorganic amendments such as vermiculite and zeolite provide surfaces for adsorption of HMs. A recent study has shown that pH change-induced soil immobilization (dolomite, steel slag, and lime) was more effective than sorption agents (zeolite and compost) in reducing plant uptake of Cd

and Pb in rice grains grown in a contaminated paddy soil [146]. Another study confirmed that pH control was the management option most likely to reduce phytoavailable Cd and Pb, since organic matter content and oxalate extractable sesquioxides only partially influenced HM retardation (K_d) [147].

Although, phosphates have been identified as a source of HMs in agricultural soils, they are widely used to immobilize metals due to their strong affinity for metals [148-150]. Phosphate was able to reduce plant uptake of metals by maize and reduce plant uptake of Pb, Cd and Zn by vegetables [151-153]. Recently, it has been shown that the application of phosphate fertilizer and lime was more effective than sawdust in reducing metal uptake by lettuce, especially for Cu and Pb [8].

Crop-Hyper accumulating plant rotation: Hyper accumulating plants are plants that are able to tolerate and accumulate HMs above standard concentrations in their above ground biomass. They can be used to reduce contaminant levels in contaminated farmlands by planting them ahead of crops to be grown on the farm. Hyper accumulating plants may be planted for about one or two years before the land is cultivated with food crops again. Selection of hyper accumulating plant to be used in phytoextraction will depend on the primary contaminant in the soil. Plants that are tolerant to multiple metal (loid)s will be particularly useful in soils contaminated with more than one contaminant.

About 500 plant species have been reported to accumulate HMs [154]. One of them, the arsenic hyper accumulator, *Pteris vittata*, has been used to reduce contaminant levels in arsenic contaminated soils [155-157]. The fern can also be used in multi-metal contaminated soils because it is tolerant to a wide variety of metals such as Pb, Cd, Zn, Se, Si, Sb, B and Hg [158-161].

There was a 3.5–11.4% reduction in the total soil as when the fern was grown in five contaminated paddy soils over a nine month period [162]. Results showed that As concentrations in the straw and grain of rice grown following *P. vittata* decreased by 17–82% and 22–58% respectively, suggesting that the fern reduced bioavailable As in contaminated paddy soils probably due to high uptake of As by the fern [162].

The Cd/Zn hyper accumulator *Thlaspi caerulescens* can be used in Cd/Zn contaminated soils though it's sensitive to Cu [163]. Hence, it cannot be used in soils with high levels of Cu. Multi-metal hyper accumulating plant such as *Ipomea spp* can accumulate Cd, Cu, Mn and Zn showing potentials to be used in multi-metal contaminated soils [163]. *Helianthus annuus* and *Hemidesmus indicus* have both been shown to be Pb hyper accumulating plant species and can be used in Pb contaminated soils [164].

Plants that are tolerant but accumulate HMs only in the roots can also be used for stabilization of HMs in contaminated soils. Eight plant species, *Alternanthera philoxeroides, Artemisia princeps, Bidens frondosa, Bidens pilosa, Cynodon dactylon, Digitaria sanguinalis, Erigeron canadensis*, and *Setaria plicata* were recently

identified as good candidates for stabilization of Mn, Cd, Pb and Zn contaminated sites [165]. Plants suitable for stabilization should have an extensive root system and keep the translocation of metal (loid)s from roots to shoots as low as possible in soils with high HM concentrations [166].

Plant varieties with low translocation of HMs from root to shoot can also be selected for cultivation in metal contaminated soils. Leafy vegetables namely, spinach, amaranthus and mustard seem to be unsafe and not suitable for cultivation on heavy metal contaminated soil while fruit type vegetables could be suggested for cultivation on Cd contained soil [167]. Alfalfa, field pumpkin, and barley had the highest Cu concentration in their roots suggesting they could be good candidates for stabilization of copper contaminated soils. But alfalfa and field pumpkin also accumulated Zn in the leaves indicating they may not be good for stabilization of Zn contaminated soils [168].

The efficiency of hyper accumulating plants can be increased by the addition or stimulation of soil microorganisms in metal contaminated soil. Soil microorganisms support the establishment and growth of plants on HM contaminated soils by producing plant growth hormones, inducing siderophores, solubilizing phosphorus; they increase the bioavailability of metals for plant uptake by hyper accumulating plants and reduce the level of growth inhibiting stress hormone in plants growing in metal contaminated soils [169].

Heavy metal (loid) resistant microbes: HM resistant soil microorganisms can be used to convert both organic and inorganic contaminants to less toxic forms. The method is more widely used to break down toxic complex organic compounds to nontoxic simpler forms. HMs cannot be broken down, so the method has its limitations. HM resistant microbes reduce the toxicity of HMs by converting them from a toxic oxidation state to nontoxic oxidation state or converting them from the more plant available fractions to the less available fractions. These transformations involve redox reactions, precipitation, and sorption and desorption reactions.

The reduction of Cr (VI) to Cr (III) is a detoxification pathway because Cr (VI) is more toxic than Cr (III). In addition, Cr (VI) is more bioavailable than Cr (III) at high pH; hence, the reduction of Cr (VI) to Cr (III) reduces its mobility in contaminated soils [170]. An indigenous actinomycete, *Streptomyces sp. MC1* was able to reduce up to 94% of the Cr (VI) after 7 days of incubation showing almost complete Cr (VI) removal from soil without any previous treatment [171].

The addition of bacteria to chromium contaminated soils led to a drastic decrease in water soluble, exchangeable and carbonate bound Cr (VI) while there was an increase in carbonate-bonded Cr(III), Fe and Mn oxides-bonded Cr(III) and organic matter-bonded Cr(III) (Li et al., 2013) [172]. This shows that the more available fractions of the more mobile Cr (VI) were converted to the less mobile fractions by soil microorganisms.

Sulfate reducing bacteria reduced the concentrations of the exchangeable fraction of Cd by 70% while the Fe-Mn oxides

and carbonate fractions increased in Cd contaminated soils [173]. *Rhodobacter sphaeroides* reduced Pb phytoavailability to wheat seedlings by decreasing the exchangeable fraction and increasing the residual fraction. The plant available fractions were converted to less mobile fractions [174]. The bioavailability of Pb in contaminated soil was reduced by incubating with *Phanerochaete chrysosporium* and straw. The concentration of exchangeable Pb in the soil was reduced thereby reducing its toxicity [175].

Indigenous soil microflora was used for in-situ immobilization of HMs in a heavily contaminated soil in two stages. The first stage involved the solubilization and leaching of metals from the top horizon to the sub horizon due to the joint action of the soil microorganisms and leach solutions used to irrigate the soils. The dissolved contaminants were then precipitated as the insoluble forms as a result of the activity of the sulfate-reducing bacteria inhabiting the sub horizon [176].

Microbes are also used to enhance removal of HMs from the soil by leaching. Iron reducing microorganism *Desulfuromonas palmitatis* was used to induce the reductive dissolution of iron oxides and release of retained As. EDTA was also used to remove metal contaminants, such as Pb and Zn, through the formation of soluble metal chelates. Bacterial activity was found to have accelerated the removal of arsenic, which increased from the value of 35% obtained during the pure chemical treatment up to 90% in the presence of *D. palmitatis* [177].

A mercury resistant bacteria strain, SA2, was able to volatilize mercury by producing mercuric reductase enzyme. About 79% mercury in a mercury supplemented culture suspension was volatilized in 6 h showing its potential to be used in mercury contaminated soils [178]. This process reduces contaminant levels in the soil while other methods involving redox and fraction transformations limit mobility of contaminants.

Soil washing: The process of removing soil particles enriched with contaminants or using aqueous solutions to mobilize and leach the contaminants out is called soil washing [179]. Soil washing is able to permanently remove contaminants from contaminated soil and contaminants can be recycled from washing solution [180]. However, the physicochemical properties of soil may change after physical separation and chemical extraction processes, which may eventually lead to a decline in soil fertility [181].

Chemical washing of Cd contaminated paddy soils with calcium chloride solution removed 55% of Cd from the exchangeable fraction and 15% of Cd from the acid-soluble fraction. Even though soil washing changed the soil fertility, it could be corrected and had no effect on rice growth, but reduced the average Cd concentration in rice grains by about two-thirds compared to a control plot [182].

Ferric chloride solution has also been used for soil washing of Cd contaminated paddy soils [183,184]. Washing with $FeCl_3$ led to the formation of Cd–chloride complexes which enhances Cd extraction from the soils. Although, soil fertility was affected by soil washing with 45 mM $FeCl_3$, it had no negative effect on rice yield and lowered the Cd concentration of rice grain and rice straw [183]. In a similar study, soil washing with calcium chloride solution had no effect on growth of soybean but the seed Cd concentration decreased significantly [185]).

Soil washing has been used to effectively reduce toxicity of metal polluted garden soils by removing the plant available fractions. HM contaminated garden soil was washed with EDTA solution in a pilot-scale remediation plant. Soil washing with EDTA removed 75%, 26% and 66% of Pb, Zn and Cd, respectively, from the garden soil, while 71% of EDTA was recycled and no waste water was generated [186]. In another study, soil washing of a metal contaminated vegetable garden soil with EDTA reduced the metal burden by 80, 28 and 72% for Pb, Zn and Cd respectively. However, the treatment significantly decreased the potential soil enzyme activity and the washed soil did not recover its biological properties [187].

The major limitations of soil washing are its effects on soil health and fertility. Although the amount of readily available As in soils were reduced after soil washing with different solutions, the bioassay tests showed that the washed soils had lower seed germination, shoot growth, and enzyme activities which was attributed to the acidic pH and/or excessive nutrient contents of the washed soils [188].

The choice of soil washing solutions and their washing order are critical to ensure high removal efficiencies of metal fractions and sustain soil fertility in contaminated soils [189]. Two-step washing of Cu contaminated soil with 0.34 M citric acid and then 1500 mg L^{-1} dissolved organic matter (DOM) solution (pH 8.5) was found to be most favorable for the soil than the conventional EDTA extraction. The citric acid and DOM treatment removed 91% Cu from the topsoil while the organic matter, cation exchange capacity, plant-available nitrogen, and available phosphate content increased by 28.1%, 103%, 17.7%, and 422%, respectively [190].

The use of a degradable chelator, N, N-bis (carboxymethyl)-l-glutamic acid (GLDA), as washing solution removed 71.34%, 81.02%, and 50.95% of Cd, Pb, and Zn respectively from a polluted farmland soil. GLDA washing solution was as effective as the conventional EDTA washing, and was able to retain most of the soil nutrients [125].

Conclusion

The sources of HMs in agricultural soils include irrigation with wastewater, applications of agrochemicals, organic and inorganic amendments. Natural sources include parent material and atmospheric deposition. Proximity to mines and smelters also increases concentrations of HMs in farmlands. Partitioning of HMs in agricultural soils depends on source, soil properties and farm management practices. The availability of HMs for plant uptake depends on their fractionation within the soil. Soil properties such as pH, organic matter content, soil texture, and Fe/Mn oxide content influence the mobility of HMs in contaminated soils. pH is the major factor determining metal mobility in the soil. Acid rain, high temperature, root exudation

018

and microbial activities in the soil may increase the mobility of HMs in the soil by increasing acidity. Farm management practices such as cropping systems, tillage methods, and land use change also influences the mobility of HMs in the soil. Strategies for reducing HM mobility in contaminated farmlands include stabilization with organic and inorganic amendments, crop–hyper accumulating plant rotations, HM resistant microbes and soil washing. These techniques reduce bioavailability by removing the plant available fractions, converting mobile fractions to less available fractions and by changing contaminants to less mobile oxidation states.

References

1. Mapanda F, Mangwayana EN, Nyamangara J, Giller KE (2005) The effect of long-term irrigation using wastewater on heavy metal contents of soils under vegetables in Harare, Zimbabwe. Agriculture Ecosystems & Environment 107: 151-165. Link: https://goo.gl/YXJq1i

2. Zhao X, Dong D, Hua X, Dong S (2009) Investigation of the transport and fate of Pb, Cd, Cr (VI) and As(V) in soil zones derived from moderately contaminated farmland in Northeast China J Haz Mat 170: 570-577. Link: https://goo.gl/T3JSo8

3. Giacalone Boussen S, Soubrand M, Bril H, Ouerfelli K, Abdeljaouad S (2013) Transfer of lead, zinc and cadmium from mine tailings to wheat (Triticum aestivum) in carbonated Mediterranean (Northern Tunisia) soils. Geoderma 192: 227-236. Link: https://goo.gl/V0v81p

4. Balkhair KS, Ashraf MA (2016) Field accumulation risks of heavy metals in soil and vegetable crop irrigated with sewage water in western region of Saudi Arabia. Saudi J Biol Sci 23: S32-S44. Link: https://goo.gl/Kr9dEm

5. Chibuike GU, Obiora SC (2014) Heavy Metal Polluted Soils: Effect on Plants and Bioremediation Methods. Applied Environ. Soil Sci Link: https://goo.gl/AWJdOW

6. Rahmanian M, Habib K, Younes RD, MirHasan RS (2011) Effects of heavy metal resistant soil microbes inoculation and soil Cd concentration on growth and metal uptake of millet, couch grass and alfalfa. African J Microbiol Res 5: 403-410. Link: https://goo.gl/ur0e1X

7. Ano AO, Eke-Okoro ON, Egesi CN (2013) Heavy metals (Cd, Ni and Pb) pollution effects on cassava (Manihot esculenta Crantz) Int J Biodivers Conservation 5: 640-646. Link: https://goo.gl/lJKQc5

8. Cu NX (2015) The effects of heavy metals, phosphate, lime and sawdust on plant growth and heavy metal accumulation by lettuce. ARPN J Agric Biol Sci 10: 241-246. Link: https://goo.gl/zJ55w8

9. Liu X, Song Q, Tang Y, Li W, Xu J, et al. (2013) Human health risk assessment of heavy metals in soil–vegetable system: A multi-medium analysis Sci Total Environ 464: 530-540. Link: https://goo.gl/dFCL9O

10. Saha GC, Ali MA (2007) Dynamics of arsenic in agricultural soils irrigated with arsenic contaminated groundwater in Bangladesh. Sci Total Environ 379: 180-189. Link: https://goo.gl/UcYTvr

11. Bian B, Lv L, Yang D, Zhou L (2014) Migration of heavy metals in vegetable farmlands amended with biogas slurry in the Taihu Basin, China. Ecol Eng 71: 380-383. Link: https://goo.gl/vbvCN1

12. Tong J, Guo H, Wei C (2014) Arsenic contamination of the soil-wheat system irrigated with high arsenic groundwater in the Hetao Basin, Inner Mongolia, China. Sci Total Environ 496: 479-487. Link: https://goo.gl/nE5PSS

13. Fayiga AO, Saha U (2016 Arsenic Contamination, Exposure Routes and Public health. Evidence-based Medicine and Public Health. Link: https://goo.gl/8fjeVx

14. USEPA (2005) Best Management Practices for Pb at Outdoor Shooting Ranges. EPA- 902-B-01e001. Revised June 2005. Region 2. Link: https://goo.gl/8PJmQK

15. Wilbur S, Abadin H, Fay M, Yu D, Tencza B, et al. (2012) Toxicological Profile for Chromium. Agency for Toxic Substances and Disease Registry (US) Health Effects. Link: https://goo.gl/KX2Mnf

16. Bernard A (2008) Cadmium and its adverse effects on human health. Indian J Med Res 128: 557-64. Link: https://goo.gl/mLrNR7

17. Guillén MT, Delgado J, Albanese S, Nieto JM, Lima A, et al. (2012) Heavy metals fractionation and multivariate statistical techniques to evaluate the environmental risk in soils of Huelva Township (SW Iberian Peninsula). J Geochemical Exploration 120: 32-43. Link: https://goo.gl/r3OYfj

18. Nicholson FA, Smith SR, Alloway BJ, Carlton-Smith C, Chambers BJ (2003) An inventory of heavy metals inputs to agricultural soils in England and Wales. Sci Total Environ 311: 205-219. Link: https://goo.gl/Xk8xB4

19. Meng W, Wang Z, Hu B, Wang Z, Li H, et al. (2016) Heavy metals in soil and plants after long-term sewage irrigation at Tianjin China: A case study assessment. Agric Water Manag 171: 153-161. Link: https://goo.gl/36OCZd

20. Amin N, Hussain A, Alamzeb S, Begum S (2013) Accumulation of heavy metals in edible parts of vegetables irrigated with waste water and their daily intake to adults and children, District Mardan, Pakistan. Food Chem 136: 1515-1523. Link: https://goo.gl/LRdQFG

21. Neidhardt H, Norra S, Tang X, Guo H, Stüben D (2012) Impact of irrigation with high arsenic burdened groundwater on the soil-plant system: Results from a case study in the Inner Mongolia, China. Environ Pollut 163: 8-13. Link: https://goo.gl/gmGl0q

22. Assadian NW, Esparza LC, Fenn LB, Ali AS, Miyamoto S, et al. (1998) Spatial variability of heavy metals in irrigated alfalfa fields in the upper Rio Grande River basin. Agric Water Manag 36: 141-156. Link: https://goo.gl/WfcDPk

23. Liu G, Tao L, Liu X, Hou J, Wang A, et al. (2013) Heavy metal speciation and pollution of agricultural soils along Jishui River in non-ferrous metal mine area in Jiangxi Province, China. J Geochem. Exploration 132: 156-163. Link: https://goo.gl/wRqfG3

24. Mileusnić M, Mapani B, Kamona A, Ružičić S, Mapaure I, et al. (2014) Assessment of agricultural soil contamination by potentially toxic metals dispersed from improperly disposed tailings, Kombat mine, Namibia. J Geochem Explor 144: 409-420. Link: https://goo.gl/IMq5Mg

25. Gebrekidan A, Weldegebriel Y, Hadera A, Van der Bruggen B (2013) Toxicological assessment of heavy metals accumulated in vegetables and fruits grown in Ginfel river near Sheba Tannery, Tigray, Northern Ethiopia. Ecotoxicol Environ Safety 95: 171-178. Link: https://goo.gl/zntLqk

26. Adamu C I, Nganje TN (2010) Heavy metal contamination of surface soil in relationship to land use pattern. A case study of Benue state, Nigeria. Mater Sci Appl 1: 127-134. Link: https://goo.gl/wJ0mRx

27. Akinnifesi TA, Asubiojo OI, Amusan AA (2006) Effects of fungicide residues on the physico-chemical characteristics of soils of a major cocoa producing area of Nigeria. Sci Total Environ 366: 876-879. Link: https://goo.gl/6oA0es

28. Lambert R, Grant C, Sauvé S (2007) Cadmium and zinc in soil solution extracts following the application of phosphate fertilizers. Sci Total Environ 378: 293-305. Link: https://goo.gl/6BxTCx

29. Yang P, Mao R, Shao H, Gao Y (2009)The spatial variability of heavy metal distribution in the suburban farmland of Taihang Piedmont Plain, China. Comptes Rendus Biologies 332: 558-566. Link: https://goo.gl/9mzkif

30. Xu X, Zhao Y, Zhao X, Wang Y, Deng W (2014) Sources of heavy metal pollution in agricultural soils of a rapidly industrializing area in the Yangtze Delta of China. Ecotoxicol. Environ Safety 108: 161-167. Link: https://goo.gl/TseuIA

31. Luo Z, Gao M, Luo X, Yan C (2016) National pattern for heavy metal contamination of topsoil in remote farmland impacted by haze pollution in China. Atmospheric Res 170: 34-40. **Link:** https://goo.gl/7ezF8S

32. Ferri R, Hashim D, Smith D, Guazzetti S, Donna F, et al. (2015) Metal contamination of home garden soils and cultivated vegetables in the province of Brescia, Italy: Implications for human exposure. Sci Total Environ 519: 507-517. **Link:** https://goo.gl/SN7WuW

33. Gu Y, Li Q, Fang J, He B, Fu H, et al. (2014) Identification of heavy metal sources in the reclaimed farmland soils of the pearl river estuary in China using a multivariate geostatistical approach. Ecotoxicol Environ Safety 105: 7-12. **Link:** https://goo.gl/8EHn0w

34. Lu A, Wang J, Qin X, Wang K, Han P, et al. (2012) Multivariate and geostatistical analyses of the spatial distribution and origin of heavy metals in the agricultural soils in Shunyi, Beijing, China. Sci Total Environ 425: 66-74. **Link:** https://goo.gl/Pk3nK0

35. Liu Y, Wang H, Li X, Li J (2015) Heavy Metal Contamination of Agricultural Soils in Taiyuan, China. Pedosphere 25: 901-909. **Link:** https://goo.gl/c9sPlj

36. Garelick H, Jones H, Dybowska A, Valsami-Jones E (2008) Arsenic pollution sources. Rev Environ Contam Toxicol 197: 17-60. **Link:** https://goo.gl/9aJRf8

37. Fayiga AO, Ma LQ (2007) Effects of plant arsenic uptake and presence of metals on arsenic distribution in an arsenic contaminated soil. Environ Pollut 147: 737-742. **Link:** https://goo.gl/uSpmfv

38. Tessier A, Campbell P, Bisson M (1979) Sequential extraction procedure for the speciation of heavy metals. Anal Chem 51: 844-861. **Link:** https://goo.gl/blhe6Z

39. Ure AM, Quevauviller Ph, Muntau H, Griepink B (1992) B. EUR report. CEC Brussels, 14763, 85.

40. Ure AM, Quevauviller PH, Muntau H, Griepink B (1993) Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the commission of the European communities. Int. J. Environ Anal Chem 51: 135–151. **Link:** https://goo.gl/nXuzRn

41. Zimmerman A, Weindorf D (2010) Heavy Metal and Trace Metal Analysis in Soil by Sequential Extraction: A Review of Procedures. Int J Anal Chem **Link:** https://goo.gl/DX3165

42. Žemberyová M, Barteková J, Hagarová I (2006) The utilization of modified BCR three-step sequential extraction procedure for the fractionation of Cd, Cr, Cu, Ni, Pb and Zn in soil reference materials of different origins. Talanta 70: 973-978. **Link:** https://goo.gl/RckTqo

43. Onken BM, Adriano DC (1997) As availability in soil with time under saturated and subsaturated conditions. Soil Sci Soc Am J 61: 746-752. **Link:** https://goo.gl/EPsuzs

44. Yang S, Zhou D, Yu H, Wei R, Pan B (2013) Distribution and speciation of metals (Cu, Zn, Cd, and Pb) in agricultural and non-agricultural soils near a stream upriver from the Pearl River, China. Environ Pollut 177: 64-70. **Link:** https://goo.gl/adqW4k

45. Fitamo D, Itana F, Olsson M (2007) Total Contents and Sequential Extraction of Heavy Metals in Soils Irrigated with Wastewater, Akaki, Ethiopia. Environ Manag 39: 178-193. **Link:** https://goo.gl/lgZl77

46. Giacalone A, Gianguzza A, Orecchio S, Piazzese D, Dongarra G, et al. (2005) Metals distribution in the organic and inorganic fractions of soil: a case study on soils from Sicily. Chemical Speciation and Bioavailability 17: 83-93. **Link:** https://goo.gl/rb19aR

47. Zhang H, Luo Y, MakinoT, Wu L, Nanzyo, M (2013) The heavy metal partition in size-fractions of the fine particles in agricultural soils contaminated by waste water and smelter dust. J Haz Mat 249: 303-312. **Link:** https://goo.gl/ZKWcTq

48. Song J, Guo Z, Xiao X, Miao X, Wang F (2009) Environmental availability and profile characteristics of arsenic, cadmium, lead and zinc in metal-contaminated vegetable soils. Transactions of Nonferrous Metals Society of China 19: 765-772. **Link:** https://goo.gl/7xMBXu

49. Sungur A, Soylak M, Ozcan H (2014) Investigation of heavy metal mobility and availability by the BCR sequential extraction procedure: relationship between soil properties and heavy metals availability. Chemical Speciation & Bioavailability 26: 219-230. **Link:** https://goo.gl/cxN061

50. Achiba W, Lakhdar A, Gabteni N, Laing G, Verloo M, et al. (2010) Accumulation and fractionation of trace metals in a Tunisian calcareous soil amended with farmyard manure and municipal solid waste compost. J Haz Mat 176: 99-108. **Link:** https://goo.gl/0OZu5D

51. Ran J, Wang D, Wang C, Zhang G, Zhang H (2016) Heavy metal contents, distribution, and prediction in a regional soil–wheat system. Sci Total Environ 544: 422-431. **Link:** https://goo.gl/uNkVsI

52. Niu L, Yang F, Xu C, Yang H, Liu W (2013) Status of metal accumulation in farmland soils across China: From distribution to risk assessment. Environ Pollut 176: 55-62. **Link:** https://goo.gl/lXUIHB

53. Bolan N, Makino T, Kunhikrishnan A, Kim P, Ishikawa S, et al. (2013) Cadmium Contamination and Its Risk Management in Rice Ecosystems, In: Donald L. Sparks, Editor(s). Advances in Agronomy 119: 183-273. **Link:** https://goo.gl/TWmjGO

54. Adamo P, Iavazzo P, Albanese S, Agrelli D, De Vivo B (2014) Bioavailability and soil-to-plant transfer factors as indicators of potentially toxic element contamination in agricultural soils. Sci Total Environ 501: 11-22. **Link:** https://goo.gl/Ux1xN7

55. Li JE, Yang XE, He ZL, Jilani G, Sun CY, et al. (2007) Fractionation of lead in paddy soils and its bioavailability to rice plants. Geoderma 141: 174-180. **Link:** https://goo.gl/cJvjjF

56. Chukwuma C (1995) Evaluating baseline data for copper, manganese, nickel and zinc in rice, yam, cassava and guinea grass from cultivated soils in Nigeria. Agriculture, Ecosystems & Environment 53: 47-61. **Link:** https://goo.gl/yzoGC1

57. Wang X, Shan X, Zhang S, Wen B (2004) A model for evaluation of the phytoavailability of trace elements to vegetables under the field conditions. Chemosphere 55: 811-822. **Link:** https://goo.gl/HIzN10

58. Meers E, Samson R, Tack F, Ruttens A, Vandegehuchte M, et al. (2007) Phytoavailability assessment of heavy metals in soils by single extractions and accumulation by Phaseolus vulgaris Environ Exp Botany 60: 385-396. **Link:** https://goo.gl/h648DR

59. Lavado R, Rodríguez M, Alvarez R, Taboada M, Zubillaga M (2007) Transfer of potentially toxic elements from biosolid-treated soils to maize and wheat crops. Agriculture Ecosystems & Environment 118: 312-318. **Link:** https://goo.gl/7I1DJd

60. Pinto E, Almeida A, Ferreira I (2015) Assessment of metal (loid)s phytoavailability in intensive agricultural soils by the application of single extractions to rhizosphere soil. Ecotoxicol Environ Safety 113: 418-424. **Link:** https://goo.gl/6Gk5gj

61. Bhattacharyya P, Chakraborty A, Chakrabarti K, Tripathy S, Powell M (2005) Chromium uptake by rice and accumulation in soil amended with municipal solid waste compost. Chemosphere 60:1481-1486. **Link:** https://goo.gl/OWKwzp

62. Malandrino M, Abollino O, Buoso S, Giacomino A, La Gioia C, et al. (2011) Accumulation of heavy metals from contaminated soil to plants and evaluation of soil remediation by vermiculite. Chemosphere 82: 169-178. **Link:** https://goo.gl/WVpcFV

63. Collin B, Doelsch E (2010) Impact of high natural soil borne heavy metal concentrations on the mobility and phytoavailability of these elements for sugarcane. Geoderma 159: 452-458. Link: https://goo.gl/3isZUw

64. Mendoza J, Garrido T, Castillo G, Martin N (2006) Metal availability and uptake by sorghum plants grown in soils amended with sludge from different treatments. Chemosphere 65: 2304-2312. Link: https://goo.gl/zfJcZV

65. Obrador A, Alvarez J, Lopez-Valdivia L, Gonzalez D, Novillo J (2007) Relationships of soil properties with Mn and Zn distribution in acidic soils and their uptake by a barley crop. Geoderma 137: 432-443. Link: https://goo.gl/jMMuYI

66. Li S, Liu R, Wang M, Wang X, Shan H, et al. (2006) Phytoavailability of cadmium to cherry-red radish in soils applied composted chicken or pig manure. Geoderma 136: 260-271. Link: https://goo.gl/Xxd4U8

67. Tijani MN (2009) Contamination of shallow groundwater system and soil–plant transfer of trace metals under amended irrigated fields. Agric Water Manag 96: 437-444. Link: https://goo.gl/QM5U3h

68. McBride MB, Shayler HA, Spliethoff HM, Mitchell RG, Marquez-Bravo LG, et al. (2014) Concentrations of lead, cadmium and barium in urban garden-grown vegetables: The impact of soil variables. Environ Pollut 194: 254-261. Link: https://goo.gl/Sc1DPQ

69. Melo W, de Stéfani Aguiar P, Melo G, Melo V (2007) Nickel in a tropical soil treated with sewage sludge and cropped with maize in a long-term field study. Soil Biol. Biochem 39: 1341-1347. Link: https://goo.gl/3VuM8t

70. Rafiq M, Aziz R, Yang X, Xiao W, Rafiq M, et al. (2014) Cadmium phytoavailability to rice (Oryza sativa L.) grown in representative Chinese soils. A model to improve soil environmental quality guidelines for food safety. Ecotoxicol Environ Safety 103: 101-107. Link: https://goo.gl/hSV7Yg

71. Barančíková G, Makovníková J (2003) The influence of humic acid quality on the sorption and mobility of heavy metals. Plant Soil Environ 49: 565–571. Link: https://goo.gl/M9zQ2J

72. Ideriah TJK, Ikpe FN, Nwanjoku FN (2013) Distribution and Speciation of Heavy Metals in Crude Oil Contaminated Soils from Niger Delta, Nigeria. World Environment 3: 18-28. Link: https://goo.gl/l9UOGv

73. Akan J, Kolo B, Yikala B, Chellube Z (2013) Levels of some agricultural pollutants in soil samples from Biu Local Government Area of Borno State, Nigeria. Merit Res J Environ Sci Toxicol 1: 71-81. Link: https://goo.gl/iWXgKp

74. Adamczyk-Szabela D, Markiewicz J, Wolf WM (2015) Heavy Metal Uptake by Herbs. IV. Influence of Soil pH on the Content of Heavy Metals in Valeriana officinalis L. Water Air Soil Pollut 226: 106. Link: https://goo.gl/cIjEm1

75. Smith SR, Giller KE (1992) Effective Rhizombium leguminosarum bio var Trifolii present in five soils contaminated with heavy metals from long-term applications of sewage sludge or metal mine spoil. Soil Biol.Biochem 24: 781-788. Link: https://goo.gl/O36BTC

76. Rutkowska B, Szulc W, Bomze K, Gozdowski D, Spychaj-Fabisiak E (2015) Soil factors affecting solubility and mobility of zinc in contaminated soils. Int J Environ Sci Technol 12: 1687–1694. Link: https://goo.gl/CVzt53

77. Al SS, El-Saeid M, Nadeem M (2014) Effect of soil chemical and physical properties on Cd mobility studied by soil thin-layer chromatography. Curr World Environ 9. Link: https://goo.gl/TmyKMH

78. Fan T, Wang Y, Li C, He J, Gao J, et al. (2016) Effect of Organic Matter on Sorption of Zn on Soil: Elucidation by Wien Effect Measurements and EXAFS Spectroscopy. Environ Sci Technol 50: 2931–2937. Link: https://goo.gl/5lE825

79. Hernandez-Soriano MC, Jimenez-Lopez JC (2012) Effects of soil water content and organic matter addition on the speciation and bioavailability of heavy metals. Sci Total Environ 423: 55-61. Link: https://goo.gl/LsSsNR

80. Ahmed I, Helal El Aziz N, Gamal R, Shaker N, Helal A (2015) Influence of some organic ligands on the adsorption of lead by agricultural soil. Arabian J Chem. Link: https://goo.gl/WvYzDB

81. Komárek M, Tlustoš P, Száková J, Chrastný V, Balík J (2007) The role of Fe- and Mn-oxides during EDTA-enhanced phytoextraction of heavy metals. Plant Soil Environ 53: 216–224. Link: https://goo.gl/JJ6EN7

82. Zheng S, Zhang M (2011) Effect of moisture regime on the redistribution of heavy metals in paddy soil J Environ Sci 23: 434-443. Link: https://goo.gl/pgQoAM

83. Lock K, Janssen CR (2003) Influence of aging on copper bioavailability in soils. Environ Toxicol Chem 22: 1162-1166. Link: https://goo.gl/QFsMBU

84. Sayen S, Mallet J, Guillon E (2009) Aging effect on the copper sorption on a vineyard soil: Column studies and SEM–EDS analysis. J Colloid Interface Sci 331: 47–54. Link: https://goo.gl/NqfdML

85. Ma Y, Lombi E, McLaughlin M, Oliver I, Nolan A, et al. (2013) Aging of nickel added to soils as predicted by soil pH and time. Chemosphere 92: 962–968. Link: https://goo.gl/vtjrNW

86. McBride MB, Cai M (2016) Copper and zinc aging in soils for a decade: Changes in metal extractability and phytotoxicity Environ. Chem 13: 160-167. Link: https://goo.gl/5NEjP2

87. Gusiatin ZM, Kulikowska D (2016) Influence of Soil Aging and Stabilization with Compost on Zn and Cu Fractionation, Stability, and Mobility. Clean Soil Air Water 44: 272–283. Link: https://goo.gl/gVrfGL

88. Liang S, Guan D, Ren J, Zhang M, Luo J, et al. (2014) Effect of aging on arsenic and lead fractionation and availability in soils: Coupling sequential extractions with diffusive gradients in thin-films technique. J.Haz. Mat 273: 272-279. Link: https://goo.gl/Cz0aa3

89. Madzin Z, Shai-in M, Kusin F (2015) Comparing heavy metal mobility in active and abandoned mining sites at Bestari Jaya, Selangor. Procedia Environ Sci 30: 232–237. Link: https://goo.gl/ztMJGH

90. Etim EU (2016) Distribution of Soil-Bound Lead Arising from Rainfall-Runoff Events at Impact Berm of a Military Shooting Range. J Environ Protection 7: 623-634. Link: https://goo.gl/UuoI0U

91. Chen G, Zeng G, Du C, Huang D, Tang L, et al. (2010) Transfer of heavy metals from compost to red soil and groundwater under simulated rainfall conditions. J Haz Mat 181: 211–216. Link: https://goo.gl/RJyRTq

92. Liao B, Guo Z, Zeng Q, Probst A, Probst J (2007) Effects of Acid Rain on Competitive Releases of Cd, Cu, and Zn from Two Natural Soils and Two Contaminated Soils in Hunan, China. Water Air Soil Pollut 7: 151-161. Link: https://goo.gl/jQY9PR

93. Yun S, Yu C (2015) Immobilization of Cd, Zn, and Pb from Soil Treated by Limestone with Variation of pH Using a Column Test. J Chem Link: https://goo.gl/XYk7xD

94. Zheng S, Zheng X, Chen C (2012) Leaching Behavior of Heavy Metals and Transformation of Their Speciation in Polluted Soil Receiving Simulated Acid Rain. PLoS ONE 7. Link: https://goo.gl/5VDnnr

95. Thouin H, Lescure T, Gautret P, Joulian C, Le Milbeau C, et al. (2014) Influence of organic matter and microbial activities on the mobility of arsenic and metals in polluted soils. International conference on Biogeochemical Processes at Air-Soil-Water Interfaces and Environmental Protection. Link: https://goo.gl/p2KaW7

96. Violante A, Cozzolino V, Perelomov L, Caporale AG, Pigna M (2010) Mobility and biovailability of heavy metals and metalloids in soil environments. J Soil Sci Plant Nutr 10: 268-292. Link: https://goo.gl/FJoH1s

97. Wu SC, Luo YM, Cheung KC, Wong MH (2006) Influence of bacteria on Pb and Zn speciation, mobility and bioavailability in soil: A laboratory study. Environ Pollut 14: 765-773. Link: https://goo.gl/vzqNhm

98. Gadd GM (2004) Microbial influence on metal mobility and application for bioremediation. Geoderma 122: 109–119. **Link:** https://goo.gl/cFpnCT

99. Levonmaki M, Hartikainen H, Kairesalo T (2006) Effect of organic amendment and plant roots on the solubility and mobilization of lead in soils at a shooting range. J Environ Qual 35: 1026-1031. **Link:** https://goo.gl/GrMjVC

100. Bao T, Sun T, Sun L (2011) Low molecular weight organic acids in root exudates and cadmium accumulation in cadmium hyperaccumulator Solanum nigrum L. and nonhyperaccumulator Solanum lycopersicum L. African J. Biotechnol 10: 17180-17185. **Link:** https://goo.gl/SUk7nU

101. Zhao FJ, Hamon RE, McLaughlin MJ (2001) Root exudates of the hyperaccumulator Thlaspi caerulescens do not enhance metal mobilization. New Phytol 151: 613-620. **Link:** https://goo.gl/qeeTFG

102. Yang J, Pan X (2013) Root exudates from sunflower (Helianthus annuus L.) show a strong adsorption ability toward Cd(II). J. Plant Interact 8: 263-270. **Link:** https://goo.gl/nHx3k4

103. Bálint AF, Röder MS, Hell R, Galiba G, Börner A (2007) Mapping of QTLs affecting copper tolerance and the Cu, Fe, Mn and Zn contents in the shoots of wheat seedlings. Biol. Plant 51: 129-134. **Link:** https://goo.gl/nvO2K4

104. Colzi I, Doumett S, Del Bubba M, Fornaini J, Arnetoli M, et al. (2011) On the role of the cell wall in the phenomenon of copper tolerance in Silene paradoxa L. Environ Exp Bot 72: 77-83. **Link:** https://goo.gl/lreSlu

105. Liu D, Islam E, Li T, Yang X, Jin X, et al. (2008) Comparison of synthetic chelators and low molecular weight organic acids in enhancing phytoextraction of heavy metals by two ecotypes of Sedum alfredii Hance. J Haz Mat 153: 114-22. **Link:** https://goo.gl/84rSOt

106. Kim S, Lim H, Lee I (2010) Enhanced heavy metal phytoextraction by Echinochloa crus-galli using root exudates. J Biosci Bioeng 109: 47-50. **Link:** https://goo.gl/6RovhL

107. Mehes-Smith M, Nkongolo K, Cholewa E (2013) Coping Mechanisms of Plants to Metal Contaminated Soil. In Environmental Change and Sustainability. InTech. **Link:** https://goo.gl/HnJ2KU

108. Luo Q, Sun L, Hu X, Zhou R (2014) The Variation of Root Exudates from the Hyperaccumulator Sedum alfredii under Cadmium Stress: Metabonomics Analysis. PLoS ONE 9. **Link:** https://goo.gl/1xbWtf

109. Ma Y, Oliveira RS, Freitas H, Zhang C (2016) Biochemical and Molecular Mechanisms of Plant-Microbe-Metal Interactions: Relevance for Phytoremediation. Front Plant Sci 7: 918. **Link:** https://goo.gl/89hmUB

110. Ma Y, Rajkumar M, Rocha I, Oliveira RS, Freitas H (2015) Serpentine bacteria influence metal translocation and bioconcentration of Brassica juncea and Ricinus communis grown in multi-metal polluted soils. Front Plant Sci 5: 757. **Link:** https://goo.gl/huID6R

111. Rathinasabapathi B, Raman SB, Kertulis G, Ma LQ (2006) Arsenic resistant proteobacterium from the phyllosphere of arsenic hyperaccumulating fern (Pteris vittata L.) reduces arsenate to arsenite. Canadian J Microbiol 52: 695-700. **Link:** https://goo.gl/RUR3MY

112. Huang A, Teplitski M, Rathinasabapathi B, Ma, LQ (2010) Characterization of arsenic-resistant bacteria from the rhizosphere of arsenic hyperaccumulator Pteris vittata L. Canadian J Microbiol 56: 236–246. **Link:** https://goo.gl/1OQ6ys

113. Al Agely A, Sylvia DM, Ma LQ (2005) Mycorrhizae increase arsenic uptake by the hyperaccumulator Chinese Brake Fern (Pteris vittata.L) J Environ Qual 34: 2181–2186. **Link:** https://goo.gl/G9JJID

114. Trotta A, Falaschi P, Cornara L, Minganti V, Fusconi A, et al. (2006) Arbuscular mycorrhizae increase the arsenic translocation factor in the As hyper-accumulating fern Pteris vittata L. Chemosphere 65: 74-81. **Link:** https://goo.gl/tGOQwp

115. Feng T, Lin H, Guo Q, Feng Y (2014) Influence of an arsenate-reducing and polycyclic aromatic hydrocarbons-degrading Pseudomonas isolate on growth and arsenic accumulation in Pteris vittata L. and removal of phenanthrene. Int Biodeterior Biodegrad 94: 12-18. **Link:** https://goo.gl/ac25pc

116. Xu C, Chen X, Duan D, Peng C, Le T, et al. (2015) Effect of heavy-metal-resistant bacteria on enhanced metal uptake and translocation of the Cu-tolerant plant. Elsholtzia splendens Environ Sci Pollut Res Int 22: 5070-5081. **Link:** https://goo.gl/PxIxuT

117. Seneviratne M, Seneviratne G, Madawala H, Iqbal M, Rajakaruna N, Bandara T, Meththika V (2015) A preliminary study of bacterial-fungal co-inoculation on heavy metal phytotoxicity in serpentine soil. Australian J. Botany 63, 261-268.

118. Islam F, Yasmeen T, Ali Q, Mubin M, Ali S, et al. (2016) Copper-resistant bacteria reduces oxidative stress and uptake of copper in lentil plants: potential for bacterial bioremediation. Environ Sci Pollut Res Int 23: 220-233. **Link:** https://goo.gl/8WIj9d

119. Sun CY, Liu JS, Wang Y, Zheng N, Wu XQ, et al. (2012) Effect of long-term cultivation on soil organic carbon fractions and metal distribution in humic and fulvic acid in black soil, Northeast China. Soil Res 50: 562–569. **Link:** https://goo.gl/oF3HFB

120. Wang G, Zhang S, Xu X, Zhong Q, Zhang C, et al. (2016) Heavy metal removal by GLDA washing: Optimization, redistribution, recycling, and changes in soil fertility. Sci Total Environ 570: 557-568. **Link:** https://goo.gl/AFl8LU

121. Ondo J, Prudent P, Massiani C, Höhener P, Renault P (2014) Effects of agricultural practices on properties and metal content in urban garden soils in a tropical metropolitan area. J Serb Chem Soc 79: 101–112 **Link:** https://goo.gl/8UY0w0

122. Wang X, Xu Y (2014) Soil heavy metal dynamics and risk assessment under long-term land use and cultivation conversion. Environ Sci Pollut. Res 22: 264-274. **Link:** https://goo.gl/jsVYD8

123. Mallmann F, Rheinheimer D, Ceretta C, Cella C, Minella J, et al. (2014) Soil tillage to reduce surface metal contamination – model development and simulations of zinc and copper concentration profiles in a pig slurry-amended soil. Agriculture Ecosystems and Environment 196: 59–68 **Link:** https://goo.gl/bExicZ

124. Mench MJ (1998) Cadmium availability to plants in relation to major long-term changes in agronomy systems. Agriculture Ecosystems and Environment 67: 175–187. **Link:** https://goo.gl/eSFz8E

125. Wang S, Wei X, Hao M (2016) Dynamics and Availability of Different Pools of Manganese in Semiarid Soils as Affected by Cropping System and Fertilization. Pedosphere 26: 351-361. **Link:** https://goo.gl/s5uezJ

126. Łukowski A, Wiater J (2009) The Influence of Mineral Fertilization on Heavy Metal Fraction Contents in Soil. Part II: Copper and Nickel. Polish J Environ Stud 18: 645-650. **Link:** https://goo.gl/lBXm47

127. Czarnecki S, Düring R (2015) Influence of long-term mineral fertilization on metal contents and properties of soil samples taken from different locations in Hesse, Germany. Soil 1: 23–33. **Link:** https://goo.gl/KP9H3A

128. Ok Y, Usman A, Lee S, El-Azeem S, Choi B, et al. (2011) Effects of rapeseed residue on lead and cadmium availability and uptake by rice plants in heavy metal contaminated paddy soil. Chemosphere 85: 677-682. **Link:** https://goo.gl/5DJLmC

129. Huang J, Hsu S, Wang S (2011) Effects of rice straw ash amendment on Cu solubility and distribution in flooded rice paddy soils. J Haz Mat 186: 1801-1807. **Link:** https://goo.gl/pojsII

130. Xu P, Sun C, Ye X, Xiao W, Zhang Q, et al. (2016) The effect of biochar and crop straws on heavy metal bioavailability and plant accumulation in a Cd and Pb polluted soil, Ecotoxicol. Environ Safety 132: 94-100. **Link:** https://goo.gl/T8qmXc

131. Cui L, Li L, Zhang A, Pan G, Bao D,et al. (2011) Biochar amendment greatly reduces rice Cd uptake in a contaminated paddy soil: A two-year field experiment. BioResources. **Link:** https://goo.gl/TbGBQB

132. Al-Wabel M, Usman A, El-Naggar A, Aly A, Ibrahim H, et al. (2015) Conocarpus biochar as a soil amendment for reducing heavy metal availability and uptake by maize plants. Saudi J Biol Sci 22: 503-511. **Link:** https://goo.gl/7l1sCp

133. Woldetsadik D, Drechsel P, Keraita B, Marschner B, Itanna F, et al. (2016) Effects of biochar and alkaline amendments on cadmium immobilization, selected nutrient and cadmium concentrations of lettuce (Lactuca sativa) in two contrasting soils. Springer Plus 5: 397. **Link:** https://goo.gl/vlxbdB

134. Shen X, Huang D, Ren X, Zhu H, Wang S, et al. (2016) Phytoavailability of Cd and Pb in crop straw biochar-amended soil is related to the heavy metal content of both biochar and soil. J Environ Manag 168: 245-251. **Link:** https://goo.gl/tjth4L

135. Singh A, Prasad S (2014) Effect of agro-industrial waste amendment on Cd uptake in Amaranthus caudatus grown under contaminated soil: An oxidative biomarker response. Ecotoxicol Environ Safety 100: 105-113. **Link:** https://goo.gl/h8ZKZv

136. Doelsch E, Masion A, Moussard G, Chevassus-Rosset C, Wojciechowicz O (2010) Impact of pig slurry and green waste compost application on heavy metal exchangeable fractions in tropical soils. Geoderma 155: 390-400. **Link:** https://goo.gl/ATmMvO

137. Clemente R, Escolar A, Bernal M (2006) Heavy metals fractionation and organic matter mineralisation in contaminated calcareous soil amended with organic materials Bioresource Technol 97: 1894-1901. **Link:** https://goo.gl/EWvK9Z

138. Zheljazkov V, Warman P (2004) Phytoavailability and fractionation of copper, manganese, and zinc in soil following application of two composts to four crops. Environ Pollut. 131: 187-195. **Link:** https://goo.gl/eGl2qP

139. Sato A, Takeda H, Oyanagi W, Nishihara E, Murakami M (2010) Reduction of cadmium uptake in spinach (Spinacia oleracea L.) by soil amendment with animal waste compost. J Haz Mat 181: 298-304. **Link:** https://goo.gl/sWWxAc

140. Mamun S, Chanson G, Benyas M, Aktar M, Lehto N, et al. (2016) Municipal composts reduce the transfer of Cd from soil to vegetables Environ Pollut 213: 8-15. **Link:** https://goo.gl/rclPQP

141. Su D, Wong J (2004) Chemical speciation and phytoavailability of Zn, Cu, Ni and Cd in soil amended with fly ash-stabilized sewage sludge. Environ Int 29: 895-900. **Link:** https://goo.gl/s6xZvc

142. Barraoui D, Labrecque M, Blais J (2008) Decontamination of sludge by the METIX-AC process. Part II: Effects on maize growth and bioaccumulation of metals. Bioresource Technol 99: 1450-1464. **Link:** https://goo.gl/6SChbc

143. Khan M, Jones D (2009) Effect of Composts, Lime and Diammonium Phosphate on the Phytoavailability of Heavy Metals in a Copper Mine Tailing Soil. Pedosphere 19: 631-641. **Link:** https://goo.gl/39l3K9

144. Lee S, Kim E, Park H, Yun J, Kim J (2011) In situ stabilization of arsenic and metal-contaminated agricultural soil using industrial by-products. Geoderma 161: 1-7. **Link:** https://goo.gl/7jACVU

145. Zhou H, Zhou X, Zeng M, Liao B, Liu L, et al. (2014) Effects of combined amendments on heavy metal accumulation in rice (Oryza sativa L.) planted on contaminated paddy soil Ecotoxicol Environ Safety 101: 226-232. **Link:** https://goo.gl/23UDHB

146. Kim S, Kim H, Seo B, Owens G, Kim K (2016) Phytoavailability control based management for paddy soil contaminated with Cd and Pb: Implications for safer rice production. Geoderma 270: 83-88. **Link:** https://goo.gl/bPdJx0

147. Lim G, Seo B, Kim K, Kim H, Kim W, et al. (2016) Transfer functions for estimating phytoavailable Cd and Pb in metal contaminated paddy and upland soils: Implications for phytoavailability based land management. Geoderma 270: 89-97. **Link:** https://goo.gl/6fUsli

148. Brown S, Christensen B, Lombi E, McLaughlin M, McGrath S, et al. (2005) An Inter-Laboratory Study to Test the Ability of Amendments to Reduce the Availability of Cd, Pb, and Zn In Situ. Environ Pollut 138: 34-45. **Link:** https://goo.gl/xgsVPY

149. Cao X, Wahbi A, Ma L, Li B, Yang Y (2009) Immobilization of Zn, Cu and Pb in Contaminated Soils using Phosphate Rock and Phosphoric Acid. J Haz Mat 164: 555-564. **Link:** https://goo.gl/obkbZt

150. Yaacoubi H, Zidani O, Mouflih M, Gourai M, Sebti S (2014) Removal of Cadmium from Water using Natural Phosphate as Adsorbent. Procedia Eng 83: 386-393. **Link:** https://goo.gl/rnl910

151. Cajuste L, Cajuste Jr L, García-OC, Cruz-DJ (2006) Distribution and Availability of Heavy Metals in Raw and Acidulated Phosphate Rock−Amended Soils. Commun Soil Sci Plant Anal 37: 2541-2552. **Link:** https://goo.gl/53lISUb

152. Wang B, Xie Z, Chen J, Jiang J, Su Q (2008) Effects of Field Application of Phosphate Fertilizers on the Availability and Uptake of Lead, Zinc and Cadmium by Cabbage (Brassica chinensis L.) in a Mining Tailing Contaminated Soil. J Environ Sci 20: 1109-1117. **Link:** https://goo.gl/KqHksx

153. Tan W, Li Z, Qiu J, Zou B, Li N, Zhuang P, Wang G (2011) Lime and Phosphate Could Reduce Cadmium Uptake By Five Vegetables Commonly Grown in South China. Pedosphere 21: 223-229. **Link:** https://goo.gl/YLSClA

154. Kramer U (2010) Metal hyperaccumulation in plants Annu Rev Plant Biol 61: 517-534. **Link:** https://goo.gl/guiiLa

155. Fayiga AO, Ma LQ (2005) Arsenic uptake by two hyperaccumulator ferns from four arsenic contaminated soils. Water Air Soil Pollut 168: 71−89. **Link:** https://goo.gl/iBxTlH

156. Gonzaga MI, Santos J, Ma LQ (2008) Phytoextraction by arsenic hyperaccumulator Pteris vittata L. from six arsenic-contaminated soils: Repeated harvests and arsenic redistribution. Environ. Pollut 154: 212-218. **Link:** https://goo.gl/vjxhV6

157. Lessl JT, Luo J, Ma LQ (2014) Pteris vittata continuously removed arsenic from non-labile fraction in three contaminated-soils during 3.5 years of phytoextraction. J Haz Mat 279: 485-492. **Link:** https://goo.gl/ufRjym

158. Fayiga AO, Ma LQ, Cao RX, Rathinasabapathi B (2004) Effects of heavy metals on growth and arsenic accumulation in the arsenic hyperaccumulator Pteris vittata L. Environ Pollut 132: 289-296. **Link:** https://goo.gl/Vx030k

159. Srivastava M, Ma LQ, Rathinasabapathi B, Srivastava P (2009) Effect of selenium on arsenic uptake in arsenic hyperaccumulator Pteris vittata L. Bioresource Technol 100: 1115−1121. **Link:** https://goo.gl/iSC1xQ

160. Wang X, Ma LQ, Rathinasabapathi B, Liu Y, Zeng G (2010) Uptake and translocation of arsenite and arsenate by Pteris vittata L.: Effects of silicon, boron and mercury. Environ Exp Bot 68: 222−229. **Link:** https://goo.gl/Iz6JPM

161. Tisarum R, Lessl JT, Dong X, de Oliveira LM, Rathinasabapathi B, et al. (2014) Antimony uptake, efflux and speciation in arsenic hyperaccumulator Pteris vittata. Environ Pollut 186: 110-114. **Link:** https://goo.gl/cfG0w7

162. Ye WM, Khan A, McGrath SP, Zhao F (2011) Phytoremediation of arsenic contaminated paddy soils with Pteris vittata markedly reduces arsenic uptake by rice. Environ Pollut 159: 3739-3743. **Link:** https://goo.gl/D8Nbzu

163. Sarma H (2011) Metal Hyperaccumulation in Plants: A Review Focusing on Phytoremediation Technology. J Environ Sci Technol 4: 118-138. **Link:** https://goo.gl/ELVIlG

164. Gratão P, Prasad M, Cardoso P, Lea P, Azevedo R (2005) Phytoremediation: green technology for the cleanup of toxic metals in the environment. Brazilian J Plant Physiol 17: 53-64. **Link:** https://goo.gl/UJiI2T

165. Yang S, Liang S, Yi L, Xu B, Cao J, et al. (2014) Heavy metal accumulation and phytostabilization potential of dominant plant species growing on manganese mine tailings. Front Environ Sci Eng 8: 394-404. **Link:** https://goo.gl/5WelpB

166. Bolan N, Park J, Robinson B, Naidu R, Huh K (2011) Phytostabilization: A Green Approach to Contaminant Containment. Advances in Agronomy 112: 145-204. **Link:** https://goo.gl/BMmdRH

167. Singh S, Zacharias M, Kalpana S, Mishra S (2012) Heavy metals accumulation and distribution pattern in different vegetable crops. J. Environ Chem Ecotoxicol 4: 170-177. **Link:** https://goo.gl/FECauN

168. Sêkara A, Poniedzialek M, Ciura J, Jêdrszczyk E (2005) Zinc and Copper Accumulation and Distribution in the Tissues of Nine Crops: Implications for Phytoremediation. Polish J Environ Studies 14: 829-835. **Link:** https://goo.gl/XZAngp

169. Egamberdieva D, Abd-Allah E, da Silva J (2016) Microbially Assisted Phytoremediation of Heavy Metal–Contaminated Soils, In Parvaiz Ahmad (Ed.) Plant Metal Interaction Elsevier 483-498. **Link:** https://goo.gl/sOkdtN

170. Avudainayagam S, Megharaj M, Owens G, Kookana RS, Chittleborough D, et al. (2003) Chemistry of chromium in soils with emphasis on tannery waste sites. Rev Environ Contam Toxicol 178: 53-91. **Link:** https://goo.gl/uTzxMF

171. Polti MA, García RO, Amoroso MJ, Abate CM (2009) Bioremediation of chromium (VI) contaminated soil by Streptomyces sp. MC1. J Basic Microbiol 49: 285-292. **Link:** https://goo.gl/DnYCQi

172. Li Q, Yang Z, Chai L, Wang B, Xiong X, et al. (2013) Optimization of Cr (VI) bioremediation in contaminated soil using indigenous bacteria. J. Cent South Univ 20: 480−487. **Link:** https://goo.gl/f49Ipn

173. Jiang W, Fan W (2008) Bioremediation of heavy metal-contaminated soils by sulfate-reducing bacteria. Ann N Y Acad Sci 1140: 446-454. **Link:** https://goo.gl/N4XVW8

174. Li X, Peng W, Jia Y, Lu L, Fan W (2016) Bioremediation of lead contaminated soil with Rhodobacter sphaeroides. Chemosphere 156: 228-235. **Link:** https://goo.gl/KXNH09

175. Huang D, Zeng G, Jiang X, Feng C, Yu H, et al. (2006) Bioremediation of Pb-contaminated soil by incubating with Phanerochaete chrysosporium and straw. J Haz Mat 134: 268-276. **Link:** https://goo.gl/2XEopc

176. Groudev S, Georgiev P, Spasova I, Nicolova M (2014) Decreasing the contamination and toxicity of a heavily contaminated soil by in situ bioremediation. J Geochemical Exploration 144: 374-379. **Link:** https://goo.gl/ih6dRW

177. Vaxevanidou K, Papassiopi N, Paspaliaris I (2008) Removal of heavy metals and arsenic from contaminated soils using bioremediation and chelant extraction techniques. Chemosphere 70: 1329-1337. **Link:** https://goo.gl/1uI9lv

178. Mahbub K, Krishnan K, Megharaj M, Naidu R (2016) Bioremediation potential of a highly mercury resistant bacteria strain Sphingobium SA2 isolated from contaminated soil. Chemosphere 144: 330-337. **Link:** https://goo.gl/OvPL1Z

179. Pearl M (2007) Understanding Soil Washing. Technical bulletin 13, CL: AIRE (Contaminated Land: Applications in Real Environments). **Link:** https://goo.gl/WzYsxQ

180. Fedje K, Yillin L, Strömvall A (2013) Remediation of metal polluted hotspot areas through enhanced soil washing – Evaluation of leaching methods. J Environ Manag 128: 489-496. **Link:** https://goo.gl/L4gKelb

181. Yi Y, Sung K (2015) Influence of washing treatment on the qualities of heavy metal contaminated soil. Ecol Eng 81: 89-92. **Link:** https://goo.gl/ILJJPt

182. Makino T, Kamiya T, Takano H, Itou T, Sekiya N, et al. (2007) Remediation of cadmium-contaminated paddy soils by washing with calcium chloride: Verification of on-site washing. Environ Pollut 147: 112-119. **Link:** https://goo.gl/fwviTO

183. Makino T, Takano H, Kamiya T, Itou T, Sekiya N, et al. (2008) Restoration of cadmium-contaminated paddy soils by washing with ferric chloride: Cd extraction mechanism and bench-scale verification. Chemosphere 70: 1035-1043. **Link:** https://goo.gl/C4A6R5

184. Makino T, Maejima Y, Akahane I, Kamiya T, Takano H, et al. (2016) A practical soil washing method for use in a Cd-contaminated paddy field, with simple on-site wastewater treatment. Geoderma 270: 3-9. **Link:** https://goo.gl/TMbMLb

185. Maejima Y, Makino T, Takano H, Kamiya T, Sekiya N, et al. (2007) Remediation of cadmium-contaminated paddy soils by washing with chemicals: Effect of soil washing on cadmium uptake by soybean. Chemosphere 67: 748-754. **Link:** https://goo.gl/bz7mKU

186. Voglar D, Lestan D (2013) Pilot-scale washing of Pb, Zn and Cd contaminated soil using EDTA and process water recycling. Chemosphere 91: 76-82. **Link:** https://goo.gl/YdxieX

187. Jelusic M, Lestan D (2014) Effect of EDTA washing of metal polluted garden soils. Part I: Toxicity hazards and impact on soil properties. Sci Total Environ 475: 132-141. **Link:** https://goo.gl/x9QYzH

188. Im J, Yang K, Jho E, Nam K (2015) Effect of different soil washing solutions on bioavailability of residual arsenic in soils and soil properties. Chemosphere 138: 253-258. **Link:** https://goo.gl/l9Blsv

189. Wei M, Chen J, Wang X (2016) Removal of arsenic and cadmium with sequential soil washing techniques using Na_2EDTA, oxalic and phosphoric acid: Optimization conditions, removal effectiveness and ecological risks. Chemosphere 15: 252-261. **Link:** https://goo.gl/5BruVc

190. Liu C, Lin Y (2013) Reclamation of copper-contaminated soil using EDTA or citric acid coupled with dissolved organic matter solution extracted from distillery sludge. Environ Pollut 178: 97-101. **Link:** https://goo.gl/9sL6wn