Soil Mineralogical Perspective on Immobilization/Mobilization of Heavy Metals

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Abstract

Knowledge on the fate and transport of heavy metals is essential for predicting the environmental impact of metal contamination on agricultural soils. This chapter presents an overview of various factors that are involved in controlling the retention and mobility of heavy metals in soils with a special reference to soil mineralogy. The bioavailability of most elements, in particular heavy metals, in soils is governed by adsorption-desorption, complexation, precipitation and ion-exchange processes. The most important surfaces involved in metal adsorption in soils are active inorganic colloids such as clay minerals, oxides and hydroxides of metals, metal carbonates and phosphates and organic colloids. In addition to soil mineralogy, other important parameters controlling heavy metal retention and their distribution are soil texture, structure, pH, redox condition, cation and anion concentration, ionic strength, organic matter, microbial and root activity and climatic conditions. However, the ultimate fate of elements depends on a combination of several factors that are working together in the soil system. Finally, several remediation strategies have also been highlighted based on the fundamental principles of metal immobilization on mineral containing soil amendments.

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4.1 Introduction

The concern over the ever-growing imbalance in the natural environments has been increasing over the last few decades. Lately, the threat of toxicity of heavy metals to plants and humans has become manifold due to environmental contamination resulting from the extensive use of heavy metals in industry and agriculture. Since soils are, inadvertently, the ultimate victim of all human activities, it is extremely important for us to protect soils from being degraded in order to give future generations a safe and sound habitat. In the order of the abundance of various metals, Pb, Cr, As, Zn, Cd, Cu and Hg are found in the contaminated sites (USEPA 1996; Wuana and Okieimen 2011). The harmful effects of these metals in posing human and animal health issues are well known. Most of these metals impose serious risk due to their potential bioaccumulation and biomagnification in the food chain. Depending on their chemical speciation the metals can even migrate into the ground water and create a more serious issue.

More than one heavy metal can co-exist in contaminated soils. The bioavailability of the metals present in such multi-element environments is regulated to a large extent by the competition for available adsorption sites. In other words, the bioavailability and bioaccessibility of heavy metals depend on the elements' interaction with various soil components which control the metals' retention and mobility in soils. Studies have demonstrated that numerous physical, chemical, biological factors can be involved in controlling the retention and mobility of heavy metals. This chapter aims to present an overview on these factors in relation to the mineralogical properties of soils. Several remediation strategies have also been highlighted based on the fundamental principles of metal immobilization on soil minerals.

4.2 Adsorption of Heavy Metals on Soil Minerals

The fate and bioavailability of most elements, in particular heavy metals, in soils is governed by adsorption–desorption processes. Their adsorption on soils and minerals are also different due to their hydrolysis behaviour (Naidu et al. 1998). Among various heavy metals, Cu and Pb are reportedly the least mobile, whereas Cd and Zn are considerably more mobile. In addition, highly toxic metalloids such as As, Cr and Se, which exist as anions in the environment, are highly mobile because these anionic species get repelled by the intrinsically negatively charged soil particles.

The adsorption of heavy metals on purified soil clay minerals has been studied extensively in the past (Sen Gupta and Bhattacharyya 2012; Bhattacharyya and Gupta 2008; García-Sánchez et al. 1999). Several chemical modification processes were also known to increase the adsorption capacity of heavy metals on clay minerals (Bhattacharyya and Gupta 2008; Sarkar et al. 2010, 2012, 2013a; Rusmin et al. 2015; Perelomov et al. 2016; Celis et al. 2000). The surfaces of clay minerals contain two major types of reaction sites, namely Bronsted and Lewis acid sites, and ion exchange sites. This could be further explained by a constant capacitance model that assumes two kinds of binding sites (Schindler et al. 1987; Angove et al. 1998). The first type of adsorption sites adsorb metals by ion exchange, whereas the second type of adsorption sites involve inner-sphere binding to ampholytic –OH groups. The hydroxyl groups located on the edges (due to silanol and aluminol groups) are responsible for many metal–clay interactions. The 1:1 type clay mineral (e.g., kaolinite) contains a net zero layer charge, but the small negative charge at the broken edges can participate in metal adsorption. Contrarily, 2:1 type clay minerals (e.g., montmorillonite) hold a net negative charge of 0.8 unit per unit cell, which makes it a better adsorbent of heavy metal cations.

Adsorption reactions involving heavy metals are extremely rapid whereas desorption reactions can be orders of magnitude slower (McBride 1994). Additionally, adsorption–desorption reactions are often not completely reversible and this non-singularity or hysteresis can increase with increased residence time (or ageing) between the heavy metal and soil constituent surface (Glover et al. 2002; Rezaei Rashti et al. 2014). The adsorption–desorption of heavy metals on clay minerals depend on many environmental factors which consequently influence their mobility in soils. A complete understanding of the surface sequestration process in soils and minerals helps to better evaluate the bioavailability and potential toxicity of heavy metals.

4.3 Factors Affecting Retention of Heavy Metals in Soil

Mobility of heavy metal elements and subsequent retention in soil is controlled by a sequence of processes, beginning with desorption or dissolution followed by diffusion and convection. Further retention of elements at another location occurs due to re-adsorption or precipitation reactions. The key factors that control heavy metal retention in soils are summarized in Fig. 4.1. However, the ultimate fate of the element depends on a combination of several physical, chemical, biological and climatic factors.

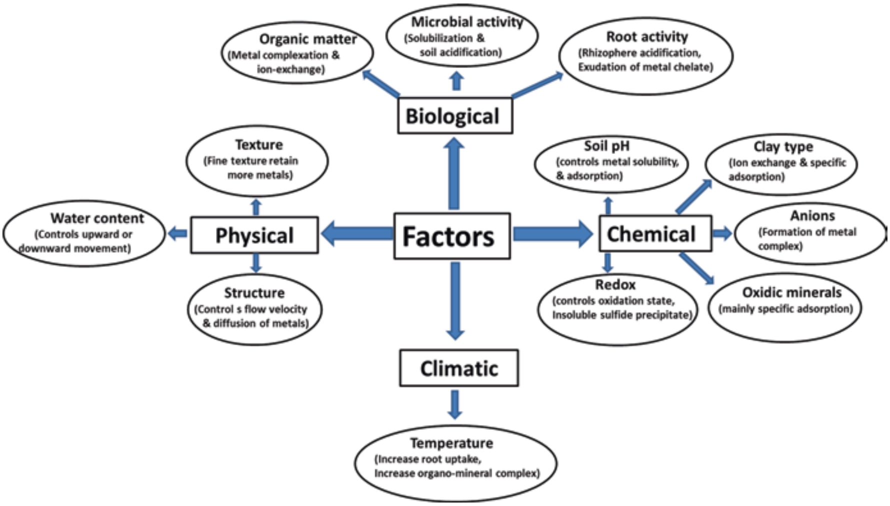

Fig. 4.1 Schematic diagram showing various factors affecting retention of heavy metals in soils

4.3.1 Physical Factors

4.3.1.1 Texture

Soil texture plays an important role in the retention of heavy metals in soils. Texture reflects the distribution of various particle size fractions including the fine particles like clay and oxidic minerals. In general, soils high in clay-sized minerals tend to retain a higher concentration of elements than coarse-textured soils, which is attributed to the higher surface area and metal binding sites of the clay-sized fraction. The importance of clays in the retention of metals was experimentally proved by several researchers. For example, Andersson (1979) demonstrated the strong adsorption affinity of Pb and other metals to the clay fractions and ranked adsorption affinity in the order of clay > silt > sand. Similarly, for a given total Cd concentration, Cd availability was higher in sandy soils than in clay soils (Eriksson 1989). In another study, the ammonium acetate extractable Zn, Pb, Cu and Cd was always lower in loamy soils than in sandy soils (Scokart et al. 1983).

4.3.1.2 Structure

The soil physical structures which may influence metal mobility include the properties such as fracturing and permeability (Jones and Jarvis 1981). This plays a crucial role in maintaining flow velocity into and out of soil aggregates which may be helpful to predict diffusion of metal ions within the soils. For example, soils with a higher macro porosity and colloids with greater surface charge contributed a higher degree of Pb mobility and transport (Karthanasis 2001). While the presence of earthworms that tended to increase soil porosity and diffusivity resulted in increased plant-available Pb and Zn concentrations (Ireland 1975).

4.3.1.3 Water Content

High solubility of heavy metals is not manifested as significant mobility unless there is sufficient water movement in the soil pores. Under arid climatic condition, the net water flow through the soil profile is upward and the mobile metals that are carried to the surface become concentrated by evaporation. Conversely, under wet condition, mobile metals are carried downward as long as there is free drainage. However, the mobility of elements is ultimately governed by the individual character of the particular elements. Agricultural sites that were subjected to the use of arsenate, lead and copper as pesticides many decades ago still retained Pb and Cu in the soil surface, although arsenate moved deeper in the soil profile in some cases (McBride 1994). Even under continuous leaching, removal of a large portion of these less mobile elements by natural process could take over thousands of years (McBride 1994).

4.3.2 Chemical Factors

4.3.2.1 Soil Reaction (pH)

Soil pH is generally considered to be the principal factor controlling elemental mobility. It governs elemental availability mainly by three ways: (1) by influencing the metal solubility; (2) controlling the precipitation–dissolution reaction, and (3) controlling the adsorption process. In general, the solubility of metals tends to increase at lower soil pH and decrease at higher pH values (Chuan et al. 1996; Ming et al. 2016). For metal cations, high pH would favor adsorption and precipitation as oxides, hydroxides and carbonates (Park et al. 2011a). Generally, in acidic pH, adsorption reaction becomes the important process in controlling elemental concentration in soil solution, whilst precipitation reaction takes the lead under alkaline conditions. Increasing solution pH tends to increase in the net negative charge of soil colloids and thus increases affinity of soils for metal cations (Naidu et al. 1998; Wu et al. 2003). The correlation between metal adsorption and pH is partly due to the competition of H^+ (and Al^{3+}) ions for binding sites at low pH leading to decreased metal adsorption (Basta and Tabatabai 1992).

4.3.2.2 Redox Condition

Soil redox potential is also crucial in controlling mobility of elements. Reduction–oxidation (redox) reaction is a process that involves flow of electrons from a reducing agent to an oxidizing agent. Redox reactions are governed by the free electron activity (pE) in soil solution, also expressed as Eh, the redox potential (Sposito 1983). High redox potential is recorded in well-aerated dry soils, whilst soils prone to waterlogging and high in organic matter content tend to have low Eh values. Some elements become more soluble and mobile in one oxidation state than another (e.g., Mn, Cr, As and Se) (Sarkar et al. 2012, 2013b). Transition metals (e.g., Fe, Mn) could facilitate the electron transfer reactions in the presence of organic acids and clay minerals to carry out reduction of metalloids (e.g., Cr) (Sarkar et al. 2013b). The elements that are classified as chalcophiles (e.g., Cu, Hg, Zn, Cd, As, Se and Pb) might form sulfide minerals in reducing environments which are insoluble in nature. The solubility of Pb, Cd and Zn could increase under reduced soil environment due to possible dissolution of Fe–Mn oxyhydroxides under reducing environments (McBride 1994). Under reducing environments Hg could form volatile organomercury compounds which might reduce soil bioavailability apparently.

4.3.2.3 Clay Content and Type

Heavy metals are less mobile in soils where a large quantity of binding sites for adsorption is available. Clay particles have surface functional groups that tend to adsorb heavy metal ions and make it immobile in nature. As described earlier, heavy metal adsorption can be described in two basic processes: nonspecific adsorption or ion exchange reaction and chemisorbed inner-sphere complex. Most phyllosilicate clay minerals such as vermiculite and montmorillonite carry permanent negative charge due to isomorphous substitution of cations within their mineral structure. A large portion of the metal binding capacity are due to the permanent and/or pH-independent charge. Further, cation adsorption by expandable layer silicates might occur largely in the inter-layer surfaces compared to the planar surfaces. However, penetration of water and metal cations between the layers of non-expandable phyllosilicates (e.g., kaolinite and serpentine) is difficult due to their low cation exchange capacity (Bhattacharyya and Gupta 2008).

4.3.2.4 Oxidic Material Content

Oxides and hydroxides of Fe and Mn occur in association with clay minerals as coatings on the phyllosilicates and also as crystals or free gels. Oxides concentrations are usually low under reducing conditions; therefore, influence of oxidic materials in controlling metal solubility is likely to be important under oxidizing environments. Hydroxides of Mn and Fe may reduce heavy metal ion concentration by both surface adsorption and precipitation reaction (Chuan et al. 1996). Surface adsorption on oxidic minerals followed by diffusion of metal ions into the small pores of mineral lattice structure might also contribute in elemental retention in soils (Backes et al. 1995). Preferential adsorptions of metals by different oxides are governed by the type of adsorbing surfaces and also by type of elements. For example, the preferential order of specific adsorption by hydrous oxides follows the order of Pb > Cu >> Zn > Cd. Oxides of Mn particularly have a strong affinity for Pb adsorption as compared to Cd. Further, Zn and Cu are probably adsorbed with equal affinity by Mn- and Fe-oxides. When multiple metals are present in the soil solutions, they might impart competition to each other for the active surfaces on clay minerals, and consequently one metal could become more mobile than the other (Ming et al. 2016).

4.3.2.5 Anions

Concentration of anions in the soil solution also controls the heavy metal solubility in soil. It is well established that various inorganic and organic anions form complexes with heavy metals and thus influences the metal solubility and subsequent mobility in soil. Precipitation of stable metal complex is governed by the type of anions present in the soil solution. For example, the mobility of Pb ions reduced in the presence of sulfate and phosphate anions due to the formation of sparingly soluble salts between Pb and these anions (Park et al. 2011a).

4.3.3 Biological Factors

4.3.3.1 Organic Matter

Organic matter affects the physical, chemical and biological conditions of soils. Decomposition of plant and animal residues leads to accumulation of organic matter in soils. Soil organic matter is composed of various functionally active compounds such as humic acid, fulvic acid and humin which are typically associated with soil inorganic colloids such as clay minerals. Organic matter reacts with heavy metals mainly by two major processes, including complexation or inner-sphere mechanism and adsorption or ion exchange reaction (Evans 1989). The active functional groups of organic matter are the negatively charged carboxyl, phenolic and amino groups that are involved in cation-binding reaction. These functional groups increase in number with the increase in humification processes. The increase in pH tends to increase in ionization of functional groups and organo-metal complexes thus become stable at higher pH values (Krishnamurti et al. 1997). There were also evidences where organic matter formed soluble organo-mineral complexes especially when organic component was dominated by the fulvic acid fraction (Temminghoff et al. 1997).

4.3.3.2 Microbial Activity

Microorganisms are considered to be the most important component controlling the biological activity in soils and influence the nutrient recycling in the system. Various functions are served by microbial transformation of metals. Generally, microbial transformation of metals is classified into two main categories: redox transformation of inorganic forms and transformations from inorganic to organic form, and vice versa (Bolan et al. 2013). Through oxidation of Mn, Fe, As and S, microorganisms can obtain energy. On the other hand, through dissimilatory reduction processes they can utilize metals as a terminal electron acceptor for anaerobic respiration. Soil microorganisms might also immobilize heavy metals by aiding the precipitation of hydrated ferric oxides and sulfides and also by exudation of metal complexing mucopolysaccharides (Park et al. 2011b). Bacterial cell walls may adsorb heavy metals from soil solutions due to the presence of surface functional groups (Mullen et al. 1989). Sometimes microorganisms might enhance metal solubility by the acidification of the soil (Ernst 1996).

4.3.3.3 Plant Root Activity

Plant root also plays an important role in controlling the metal bioavailability (Krishnamurti et al. 1997; Ernst 1996). The exudation of acidic chemicals (e.g., H_2CO_3) lowers the rhizospheric pH and hence increases metal bioavailability. Plant roots are also known to release chelating organic molecules that tend to solubilize metal cations from its insoluble forms, which results in greater bioavailability of metals in the solution. Further, symbiotic association of fungi with plant roots might facilitate metal solubilization over a large soil area.

4.3.4 Climatic Factors

Heavy metal uptake by plant roots was found to be positively correlated with temperature (Miller and Friedland 1994). This relationship was attributed to the increase rate of organic matter decomposition at higher temperature, which increased the mobilization of organo-metal complexes. Moreover, with an increase in temperature, the metal activity in the soil solutions and in plant roots might increase the absorption rate. Further, high evapo-transpiration rate at higher temperature also might contribute to an increased uptake of metals by plants.

4.4 Stabilization/Immobilization of Heavy Metals in Soils

The key mechanisms of immobilization of heavy metals in soils are adsorption, surface complexation, precipitation and ion exchange (Fig. 4.2). These are achieved by applying various amendments to the contaminated soils (Table 4.1). One of the most effective physico-chemical processes controlling the behavior and bioavailability of heavy metals is adsorption (Wan Ngah and Hanafiah 2008). A charged solute (ions) can get attached to the charged soil surface due to electrostatic interaction (Bolan et al. 2003). This strategy of immobilization involves the addition of adsorbents (e.g., clay minerals, zeolites, fly ash, red mud and biochar) into the contaminated soil (Wuana and Okieimen 2011; Sarkar et al. 2012; Antoniadis et al. 2012; Taghipour and Jalali 2015; Usman et al. 2005; Zhang et al. 2016). The adsorbent can also provide surface complexation reaction. Through this reaction metals are redistributed from solution phase to the solid phase and reduce their bioavailability in the environment (Bolan and Duraisamy 2003). In this method, functional groups like hydroxyl, carboxyl, amino and phenoxyl on the surface of organic matter or clay minerals react with heavy metals and produce surface complexes (Harter and Naidu 1995). These complexes are of two types: (1) inner-sphere complexes, in which no molecule of the solvent is interposed between surface functional groups and ions, and (2) outer-sphere complexes, in which at least one molecule of the solvent comes between the surface functional groups and ion (Alloway 1995; Bolan et al. 2014). The outer-sphere complexes are less stable than inner-sphere complexes. Precipitation of heavy metals is another way to reduce metal bioavailability in soils. Precipitation can be achieved by adding various binding agents (e.g., cement, biochar, fly ash, lime, zeolite, manure, compost, chitosan and sewage sludge) (Bolan et al. 2014; Ling et al. 2008; Wuana and Okieimen 2011; Xi et al. 2014). Precipitation of hydroxides or sulfides within the solid matrix is one of the major mechanisms by which metals can be immobilized (Fu and Wang 2011). Hydroxide precipitation is relatively effective in the pH range of 8–11 (Huisman

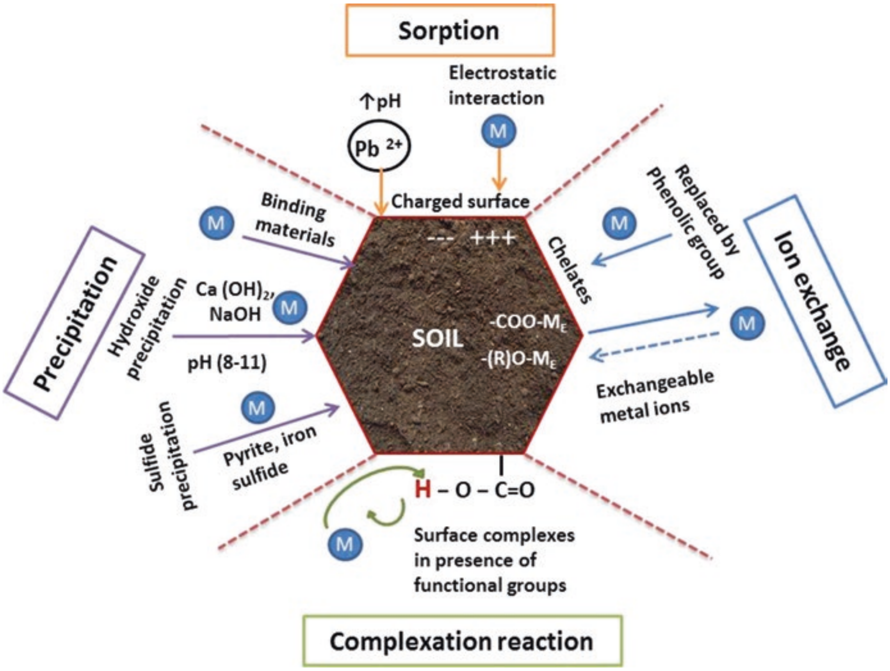

Fig. 4.2 Schematic diagram representing different immobilization/stabilization processes of heavy metals in soil

Table 4.1 Soil amendments for heavy metal immobilization

Materials	Sources	Heavy metal immobilized
Lime	Lime factory	Cd, Cu, Ni, Pb, Zn
Phosphate salt	Fertilizer plant	Pb, Zn, Cu, Cd
Hydroxyapatite	Mining of phosphate rock	Zn, Pb, Cu, Cd
Fly ash	Thermal power plant	Cd, Pb, Cu, Zn, Cr
Slag	Thermal power plant	Cd, Pb, Zn, Cr
Red mud	Aluminum industry	Zn, Cu, Cd
Clay minerals	Mining industry	Cd, Pb, Cu, Zn, Cr, As
Zeolites	Mining industry	Zn, Cd
Fe/Mn oxides	Oxidic minerals	Cd, Pb, Cu, Zn,

et al. 2006). Ion exchange is another way of remediating heavy metals in soils (Dabrowski et al. 2004). In this method, metal cations are replaced by surrounding phenolic groups, finally forming a chelate. The ion exchange agent could be naturally occurring inorganic zeolites or synthetically produced organic resins (Vazquez et al. 1994). However, this is a reversible process. Depending on the type of functional groups of exchanging ions, ion exchanger can be strongly acidic (sulfonate), weakly acidic (carboxylate), strongly basic (quaternary ammonium) and weakly basic (tertiary and secondary amines) (Hubicki and Kołodyńska 2012). Remediation

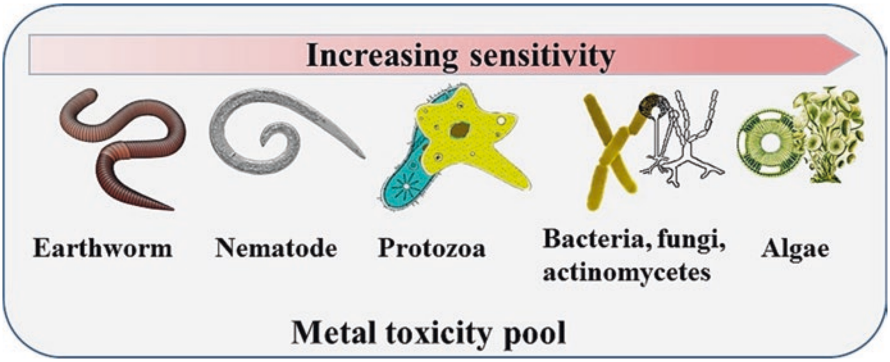

Fig. 4.3 A generalized schematic presentation of different level of toxicity of metals on various soil biota (adapted and modified from Vig et al. 2003)

of heavy metal contaminated soils with various organic and inorganic amendments has attracted attention due to the method's low cost and environmental benefits.

4.5 Biological Quality of Metal Contaminated Soils

Metals can impose highly toxic effect on the native microorganisms in soils. The microorganisms also need metal ions at very low concentration for their nutrition. However, an excess amount of these essential metals can be detrimental for their cellular functions (Lemire et al. 2013). In a soil microhabitat, the degree of metal toxicity to microorganisms depends primarily on the types of metals, their speciations and the microorganisms themselves (Giller et al. 1998). A generalized toxicity profile of heavy metals represents that microorganisms (e.g., algae, bacteria, fungi, actinomycetes and protozoa) are more vulnerable to metal toxicity than the macrobiota (e.g., nematode and earthworm) (Fig. 4.3) (Vig et al. 2003). This chapter mainly emphasizes on the microorganisms due to their major role in the dynamics of soil biogeochemical processes in agricultural and environmental remediation perspective.

The heterogeneity of soil largely controls whether the toxicity of metals is mitigated or not. As described earlier, numerous factors including soil pH, organic matter and mineralogical composition are involved. Clay minerals and some of their modified products are efficient adsorbents of toxic metals in soils. This reduces metal bioavailability to the microorganisms and saves them from toxicity (Biswas et al. 2015; Mandal et al. 2016). In soils, the microorganisms often tend to nest with or in the vicinity of clay minerals and form micro-aggregates or biofilms (Almås et al. 2005; Biswas et al. 2017; Giller et al. 2009). Therefore, the application of clay minerals (as amendments) can be an efficient supplement in soil microsites to protect the microbial cells from toxic metals.

However, the efficiency of a clay-based adsorption technique mostly lies on the properties of the clay mineral for a target toxic metal. Álvarez-Ayuso et al. (2003)

reported that a 4% palygorskite amendment in a mining soil (pH = 5.4) immobilized 92% of the mobile (soluble and exchangeable) Pb, 77% of Cu, 76% of Zn and 48% of Cd. Several other clay minerals and zeolite were also used as the metal-immobilizer in soil; however, how the addition of clay minerals into soil would impact the microbial community and thus the overall microbial quality remained inconclusive. It was found that the toxicity of Cu (in terms of substrate-induced nitrification and substrate-induced respiration) could not be explained by the soil solution metal concentrations or exchangeable metal concentrations, but a significant relationship was found between the EC_{50} values for substrate-induced respiration and percent clay content (Broos et al. 2007). Therefore, it is highly important to conduct field scale studies in the toxicological perspective for the quality of soil biota while a raw and modified clay products is used as the metal adsorbent.

4.6 Conclusions

The fate and behavior of heavy metals and metalloids in the soil environment are governed by numerous physical, chemical and biological factors. The key physico-chemical properties that control heavy metal retention in soils are imparted by the clay minerals and oxidic particles. Additionally, organic colloidal particles also play an important role. The mineral and colloidal particles have numerous active sites on their surfaces which can retain heavy metals through adsorption, complexation, precipitation and ion exchange. Due to these properties mineral amendments can be applied to contaminated soils alone or in combination with another organic amendment for immobilizing heavy metals. This can be one of the cost effective strategies for heavy metal remediation in contaminated soils. However, further research is needed to investigate the bio-physico-chemical interactions of heavy metals where microorganisms also play a key role in the biogeochemical cycle of elements in soils.

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