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REVIEW PAPER

Remediation of soils contaminated with heavy metals with an emphasis on immobilization technology

Zahra Derakhshan Nejad · Myung Chae Jung · Ki-Hyun Kim

Abstract The major frequent contaminants in soil are heavy metals which may be responsible for detrimental health effects. The remediation of heavy metals in contaminated soils is considered as one of the most complicated tasks. Among different technologies, in situ immobilization of metals has received a great deal of attention and turned out to be a promising solution for soil remediation. In this review, remediation methods for removal of heavy metals in soil are explored with an emphasis on the in situ immobilization technique of metal(loid)s. Besides, the immobilization technique in contaminated soils is evaluated through the manipulation of the bioavailability of heavy metals using a range of soil amendment conditions. This technique is expected to efficiently alleviate the risk of groundwater contamination, plant uptake, and exposure to other living organisms. The efficacy of several amendments (e.g., red mud, biochar, phosphate rock) has been examined to emphasize the need for the simultaneous measurement of leaching and the phytoavailability of heavy metals. In addition, some amendments that are used in this technique are inexpensive and readily available in large quantities because they have been derived from bio-products or industrial by-products (e.g., biochar, red mud, and steel slag). Among different amendments, iron-rich compounds and biochars show high efficiency to remediate multi-metal contaminated soils. Thereupon, immobilization technique can be considered a preferable option as it is inexpensive and easily applicable to large quantities of contaminants derived from various sources.

Z. Derakhshan Nejad · M. C. Jung (✉)
Department of Energy and Mineral Resources
Engineering, Sejong University, Seoul 05006,
South Korea
e-mail: jmc65@sejong.ac.kr

K.-H. Kim
Department of Civil and Environment Engineering,
Hanyang University, Seoul 04763, South Korea

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Graphical Abstract
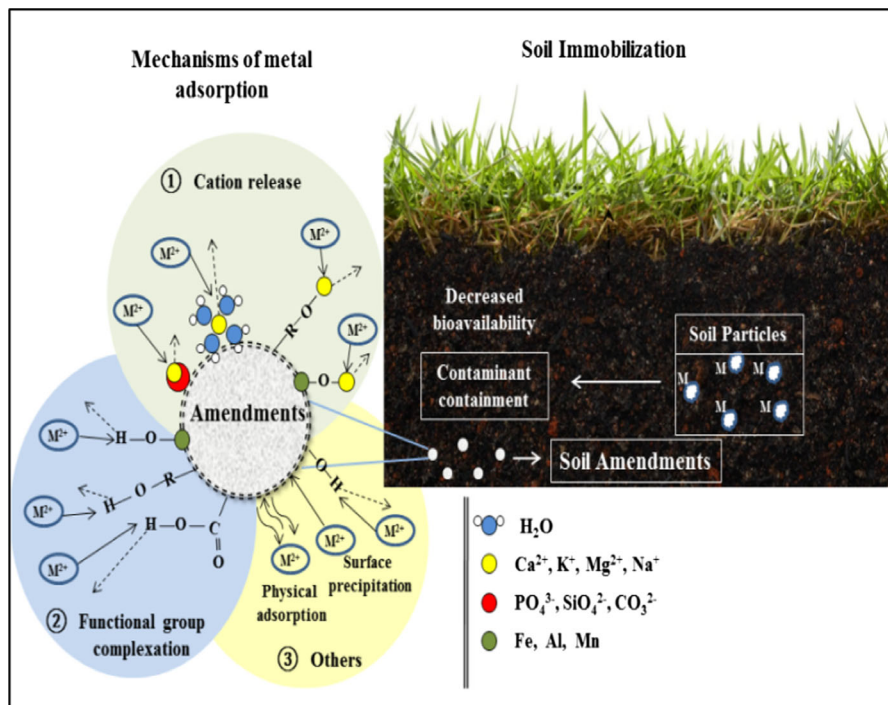
Introduction

With a widespread, rapid dissemination of contaminants like heavy metals in agricultural land, the stress on terrestrial ecosystems and societies has substantially increased (Alloway 2013; Grimm et al. 2008). Heavy metal pollution in croplands can result in enhanced dietary exposure through soil–plant–food chain transfers (Chaney et al. 2004). The prevention of heavy metals in contaminated soil is not only necessary to control the sources but also to enhance the remediation efficiency of contaminated soils (Zhou et al. 2004). A variety of remediation technologies have been developed for soil cleanup in the world (Iskandar and Adriano 1997; Stegmann et al. 2001) (Fig. 1), for example, thermal remediation for Hg (Hseu et al. 2014); soil washing for As (Ko et al. 2006); chemical leaching for Cd (Makino et al. 2007); solidification/stabilization for Zn (Al-Wabel et al.

2014); and phytoremediation for Pb (Babu et al. 2013). Key factors influencing the applicability and selection of such technologies are (1) cost, (2) long-term effectiveness/persistence, (3) commercial availability, (4) general acceptance, (5) the abundance of target metal concentrations, (6) media type (heavy metals and organics), and (7) physicochemical properties (toxicity, mobility, volume, etc.). Remediation technologies can be classified into two main groups: in situ and ex situ treatment techniques (Pare 2006; Donlon and Bauder 2008).

In situ technologies

In situ treatment of contaminated soils has considered as a potent and cost-effective ecological treatment option. It encompasses a variety of methods to treat contaminated soils without removing them from the site. However, relatively little has been done to investigate approach. In situ treatment can be divided into two areas: biological/chemical treatment methods and solidification/stabilization treatment methods. This former treatment involves the addition of microorganisms and/or chemicals to the soils to

Fig. 1 Flowchart of soil remediation technologies
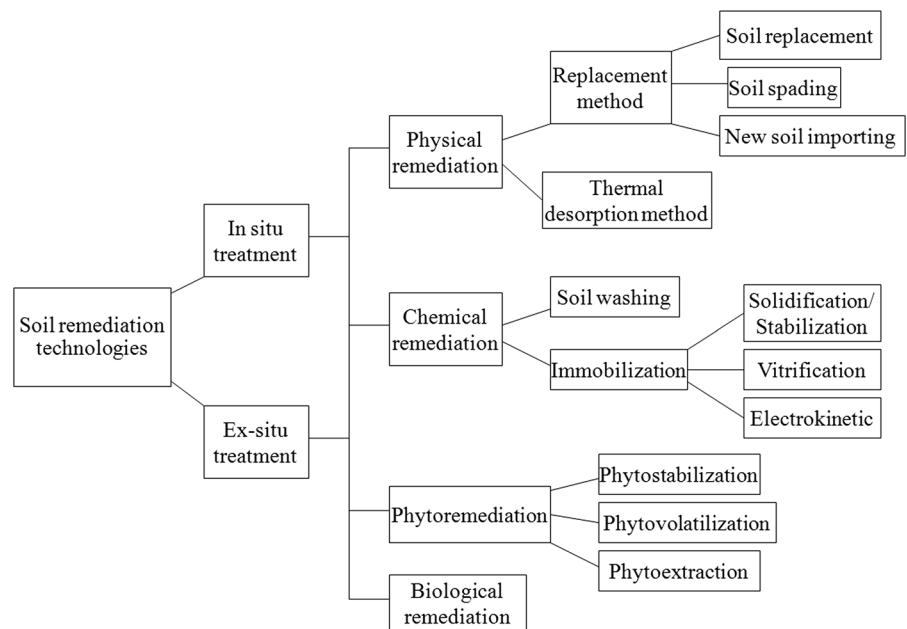
initiate or enhance bioremediation, while the latter relies on the addition of chemicals or cements (e.g., Portland cement and quicklime) to encapsulate contaminated soils and/or convert them into less soluble, less mobile, or less toxic forms. When in situ treatments are applied, soils are left in place subsequently decrease the chance of further contamination from resuspension of contaminants in which bound to the fine particles in the soils. In situ treatment technologies reduce risk of exposure and consequential spills of the soils mainly due to the low demand of handling soils. In addition, these treatments beneficially reduce the volume and mobility of hazardous substances and subsequently their volatilization and loss to the atmosphere (Renholds 1998; de Kreuk 2005). However, because of limitations such as saturated conditions, anaerobic environments, and ambient temperatures, the type of techniques used for in situ treatment is insufficiently broad compared to ex situ treatment. In general, in situ treatment appears to be less expensive than ex situ treatment or disposal of contaminated soils.

Ex situ technologies

Ex situ remediation involves excavation to treat contaminated soils elsewhere, which is not cost-effective (Kuppusamy et al. 2016). For instance, USEPA (1996)

reported the cost for in situ process (e.g., solidification/stabilization) around 32.28 \$ ton^{-1}, while Acharya (1994) evaluated 85–94 \$ ton^{-1} for the same ex situ process (S/S). Its options can be categorized into physical, chemical, electrical, thermal, and biological treatment. From this, digest physical, chemical, and electrical mechanisms have been abridged into one group, called physicochemical treatment. This treatment relies on the physical and/or chemical properties of the contaminants or the contaminated medium to destroy (i.e., chemically convert), separate, or contain the contamination (Lodolo 2014). These treatments are typically cost-effective and can be completed in short time periods (in comparison with biological treatment). Equipment is readily available and is generally neither engineering nor energy intensive. Thermal treatments offer quick cleanup times, but are typically the costliest treatment group. Cleaning soil with thermal methods may take a few months or even up to several years. Its duration depends on three major factors which can vary from site to site: (1) type and amounts of chemicals present, (2) size and depth of the polluted area, and (3) type of soil and conditions present (Lodolo 2014). Biological processes are typically implemented at low cost. However, the process requires more time and it is difficult, in general, to determine whether contaminants have been completely destroyed. Additionally, microbes are often sensitive to toxins or highly

concentrated contaminants in soil. Many genera of microbes like Bacillus, Enterobacter, Escherichia, Pseudomonas and also some fungus and yeasts help in bioremediation of heavy metals contaminated soils and water (Kotas and Stasicka 2000). Biological treatment is further divided by the phase of waste: slurry-phase or solid-phase bioremediation. The former, also known as bioreactors, is a controlled treatment that involves the excavation of the contaminated soil, mixing it with water, and placing it in a bioreactor. Solid-phase bioremediation is an ex situ technology in which the contaminated soil is excavated and placed into piles. Some solid-phase treatment processes include land farming, soil biopiles, and composting (Lodolo 2014). In situ remediation techniques are often preferable choice over ex situ option in terms of the costs of the remediation excavation and transportation (Vasile Pavel and Gavrilescu 2008). However, relatively little has been done to investigate this approach.

In this paper, to gain better knowledge, the performance of the different types of remediation techniques is reviewed with an emphasis on immobilization technique. Also, the bioavailability of heavy metals is detailed using a range of immobilizing soil amendments through manipulation. An easy-to-use summary of the important elements present in amendments that can affect the soil immobilization and implementation mechanisms in a defined set of site is also included.

Sources of heavy metal(loid)s in contaminated soils

Heavy metal(loid)s in soils are derived both from the soil parent material (lithogenic source) and various anthropogenic sources. Most heavy metal(loid)s occur naturally in soil parent materials, chiefly in forms that are not readily bioavailable for plant uptake. Heavy metals occurring naturally in the soil environment from the pedogenetic processes of weathering of parent materials are present at trace level quantities (<1000 mg kg^{-1}); hence, they are scanty toxic (Kabata-Pendias and Pendias 2001; Pierzynski et al. 2000). Unlike pedogenic inputs, heavy metal(loid)s added through anthropogenic activities typically have a high bioavailability (Lamb et al. 2009). In general, soils at industrial sites are exposed to distinct groups of heavy metal(loid) contaminants, which depend on the types of industries (and their raw materials and

products). Soils in all urban areas are generally contaminated with various metal species (e.g., Cd, Cu, Pb, Zn) due to traffic, paint and many other non-specific urban sources (Tchounwou et al. 2012; Todorovic et al. 2014). Figure 2 summarizes the frequency of metals occurring commonly in all matrices at Superfund sites. The most common metals found at contaminated sites are in the following order: lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), and mercury (Hg). The specific type of metal contamination found at the Superfund sites was seen to be directly related to the operation that took place at the sites (EPA 1996). Although the heavy metal(loid) composition of agricultural soils tends to be more closely governed by the parent materials, input from other sources (e.g., deposition of long-range transport of air pollutants (LRTAP) from fossil fuel combustion) can also contribute (Alloway 2013).

The heavy metals essentially become contaminants in the soil environments because (1) their rates of generation via manmade cycles are more rapid relative to natural ones, (2) they become transferred from mines to random environmental locations with high potential for direct exposure, (3) the concentrations of the metals in discarded products are high compared to those in the receiving environment, and (4) the chemical form (species) in which a metal is found in the receiving environmental system may render it more bioavailable (Amore et al. 2005). Note that biosolid is the major source of metal(loid) inputs in Europe and North America, while P fertilizers are identified the major source of heavy metal(loid)s
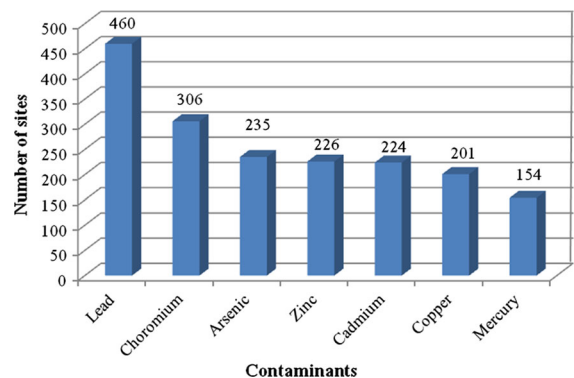

Fig. 2 Metals most commonly present in all matrices at Superfund sites (EPA 1996)

input, especially Cd, in Australia and New Zealand (Loganathan et al. 2008).

Classifications of the remediation technologies

Physical remediation

The physical remediation mainly includes soil replacement method and thermal desorption. The former relies on the use of clean soil to fully or partly replace the contaminated soil with the aim of diluting the pollutant concentration and increasing the soil environmental capacity for the remediation (Qian and Liu 2000; Zhang et al. 2001). The soil replacement method is also classified into three types: (1) soil replacement, (2) soil spading, and (3) new soil importing. Soil replacement is replacing the contaminated soil with new soil. This method is suitable for treatment of small-scale contamination. Soil spading is deeply digging the contaminated soil, inducing the pollutant spread into the deep sites to achieve dilution and natural degradation. New soil importing is adding a large amount of clean soil into the contaminated soil, covering the surface (or mixing) to reduce pollutant levels. Soil replacement can effectively isolate the soil and ecosystem, thus decreasing the effect of pollutants on environment. This technology is costly and suitable just for soil in small area (Zhou et al. 2004).

Thermal desorption heats the contaminated soil using steam, microwaves, and infrared radiation to volatilize the pollutant (e.g., Hg, As) (Li et al. 2010). According to Hseu et al. (2014), thermogravimetric method heating to 550 °C for a duration of 1 h was an effective approach for Hg removal. With the employment of thermal treatment, up to 99% of Hg could be removed (Table 1).

Chemical remediation

Chemical remediation involves the use of chemicals to extract or stabilize pollutants in contaminated media. There are several chemical remediation methods including chemical leaching (soil washing) and immobilization techniques (solidification/stabilization, vitrification, and the electrokinetic method) (Fig. 1) (Tampouris et al. 2001; Ou-Yang et al. 2010). These techniques either remove risk by chemically degrading hazardous substances or achieve stabilization of the contaminants within the bulk matrix by breaking pollutant linkages (Table 1).

Chemical leaching

Chemical leaching consists of washing the contaminated soil with fresh water, reagents, and others fluids (or gas) to leach pollutants from the soil (Tampouris et al. 2001; Ou-Yang et al. 2010). Soil washing is cost-effective because it can reduce the quantity of material that would require further treatment (by another technology). A new soil washing practice combined with on-site wastewater treatment was also introduced by Makino et al. (2007). In order to investigate Cd extraction from soils, different types of the chemicals were applied. The proportion of total soil Cd extracted by the washing chemicals (i.e., the Cd extraction efficiency) increased in the following order: Mn salts = Zn salts $\ll$ ferric Fe salts in all soils, with efficiencies of 4–41, 8–44 and 24–66%, respectively. The total Cd content of soil decreased substantially, to 55% of the unwashed value, compared to a value of 83% after $CaCl_2$ treatment in a field washing experiment. These results indicate that $FeCl_3$ has a high Cd extraction efficiency in paddy soils. Soil washing had markedly positive effects on the growth and yield of rice crops. It considerably decreased the Cd concentrations in the rice straw and unpolished rice, from 0.91 to 0.31 mg kg^{-1} in the unwashed soil to 0.18 and 0.053 mg kg^{-1} in the washed soil, respectively (Makino et al. 2007). These results proved the efficiency and effectiveness of this approach for the remediation of Cd-contaminated paddy fields. In addition, Tokunaga and Hakuta (2002) investigated the effects of different concentrations of hydrogen fluoride, phosphoric acid, sulfuric acid, hydrogen chloride, nitric acid on As extraction from artificially polluted soil (As 2830 mg kg^{-1}). It was found that phosphoric acid proved to be most promising as an extractant, attaining 99.9% arsenic extraction at 9.4% acid concentration in 6 h.

Immobilization techniques

Chemical fixation is adding reagents or materials into the contaminated soil to form insoluble or hardly movable, low toxic matters; it can thus decrease the migration of heavy metals to water, plant, and other environmental media (Zhou et al. 2004). If the soil

Table 1 Summary of heavy metal removal potential using different soil remediation technologies

Methods	Targeted metal(loid)s	Efficiency (%)	References
Physical remediation			
Thermal remediation	Hg	99% of Hg could be removed from soil	Hseu et al. (2014)
Soil washing (column test)	Cd, Zn, Cr, Pb	70, 30, 25, and 10% of Cd, Zn, Cr, Pb at neutral pH were extracted, respectively	Abumaizar and Smith (1999)
Soil washing (pilot test)	As	63–75% of As was leached out	Ko et al. (2006)
Chemical remediation			
Chemical leaching			
Using 0.1 M sodium metabisulfite + 0.01M EDTA	Cd, Zn, Pb, Cr	100, 70, 60, and 16% of Cd, Zn, Pb, Cr were extracted, respectively	Abumaizar and Smith (1999)
Using $CaCl_2$	Cd	83% of Cd was decreased after treatment	Makino et al. (2007)
Using 0.1 M hydrochloric acid	Co, As, Hg	80–90% of metals depending on temperature and time were leached out	Alghanmi et al. (2015)
Immobilization			
Using amendments			
$CaCO_3$	Zn, Cd, Pb	Flow-weighted mean concentration of Zn, Cd, and Pb were decreased by 98.5, 88.3, and 57%, respectively	Houben et al. (2012)
Iron grit	Pb	Flow-weighted mean concentration of Pb was decreased by 83%	Houben et al. (2012)
Conocarpus biochar	Mn, Cu, Cd, Zn	Reduced shoot heavy metal concentration in plants by 61–28%, respectively	Al-Wabel et al. (2014)
Phosphate rock	Cd, Pb, Cu, Zn	Reduced uptake in plant shoots by 74–14%, respectively	Zhao et al. (2014)
Vitrification	Mn, Cu, As, Fe, Ni, Zn, Hg, Pb, Cd, Cr, Se	Concentration of heavy metals after treatment ($T > 1300$ °C) reduced in leachate by almost 91–100%	Navarro et al. (2013)
Electrokinetic remediation	Cu, Pb	After treatment, 41 and 31% removal of Cu and Pb were observed (using 4–26 V as current)	Ottosen et al. (2012)
Phytoremediation			
Phytoextraction	Pb, Zn, As, Cd, Cu, Ni	Removal capacity by Alnus firma was evaluated 77–10%, respectively	Babu et al. (2013)
Phytoextraction	Pb	Efficiency process 30–80% with maximum value in *Alternanthera phyloxeroides*	Cho-Ruk et al. (2006)
Phytoextraction	Cd, Zn	Populus accumulated both Cd and Zn up to 82%	Hassinen et al. (2009)
Biological remediation			
Bioleaching	Cu, Cd, Pb, Zn	Maximum removals of 98–15% for metals were achieved. (Using a fungus Aspergillus niger)	Ren et al. (2009)
Taken up metals by microbes	Cd, Hg, Ag, Zn, Cu, Ni	170, 58, 54, 14, 15, 13% dry wt of metals were taken up by microorganisms, respectively	Rajendran et al. (2003)

immobilization technique is employed, simplicity and rapidity (besides high public acceptability) will be achieved. This method is relatively inexpensive, while covering a broad spectrum of inorganic pollutants. However, as in situ immobilization is only a temporary solution (contaminants are still in the environment), the activation of pollutants may occur when soil physicochemical properties change. Hence, the reclamation process should be applied only to the surface layer of the soil (30–50 cm), and permanent

monitoring is necessary (Martin and Ruby 2004; USEPA 1997). Different kinds of the immobilization techniques are summarized below.

Solidification/stabilization (S/S)

Solidification/stabilization, also referred to as waste fixation, was devised to reduce the mobility of hazardous substances in the environment through both physical and chemical means (Sherwood and Qualls 2001). Stabilization generally refers to the process of reducing the risk posed by a waste by converting the contaminant into a less soluble, mobile, and toxic state. The continuing solidification stage also helps to encapsulate the waste materials in a solid form (Anderson and Mitchell 2003). The application of S/S technology will be affected by the chemical composition of the contaminated matrix, the amount of water present, and the ambient temperature. These factors can interfere with the S/S process by inhibiting the bonding of the waste to the binding material, retarding the setting of the mixtures, decreasing the stability of the matrix, or reducing the strength of the solidified area (USEPA 1990). Stabilization is the general term for a process that transforms contaminants into a less mobile or toxic form, while solidification is a more specific process that treats material to increase its solidity and structural integrity. This process may be performed either ex situ or in situ. S/S technology has low cost because the reagents are widely available and inexpensive, while applicable to a variety of contaminants. This method can be applied to different types of soils as well with high throughput rates. The required equipment for its application is widely available and simple. However, in this method, contaminants are still in the soil, not destroyed or removed. Hence, volatile organic compounds and some particulates may come out during the treatment process. The other problem is long-term efficiency of the S/S which is still uncertain (Grobbel and Wang 2012).

Al-Wabel et al. (2014) investigated the impact of biochar rates (0.0, 1.0, 3.0, and 5.0% w/w) with two soil moisture levels (75 and 100% of field capacity, FC) on the immobilization and availability of Fe, Mn, Zn, Cd, Cu, and Pb to maize plants. The biochar addition through the stabilization process significantly reduced the shoot heavy metal concentrations in maize plants (except for Fe at 75% FC) in response to increasing the application rates, with a highest

decrease of 51.3 and 60.5% for Mn, 28 and 21.2% for Zn, 60 and 29.5% for Cu, and 53.2 and 47.2% for Cd at soil moisture levels of 75 FC and 100% FC, respectively. These results suggest that biochar may be effective amendment media for heavy metal stabilization and reducing its phytotoxicity. In addition, Lv et al. (2009) studied the efficiency of sodium bentonite on remediation of Cd-contaminated soil through the S/S process. The results also showed that the concentration of Cd was reduced to 21.4, 27.6, 27.2, and 32.3% as compared with the control when the additive amount was 20, 30, 50, and 40 g kg^{-1}, respectively.

Vitrification

Vitrification is the transformation of a substance into a glass. Vitrification, or molten glass, is a method of S/S that uses a powerful source of energy to "melt" soil or other earthen materials at extremely high temperatures (1600–2000 °C), immobilizing most inorganic pollutants (ESTCP 2000).

A highly attractive aspect of vitrification is that it can bind a wide variety of toxic species into a glass matrix at the atomic level and usually with a significant reduction of waste volume. The technology is a cost-effective method for difficult sites with mixed contaminants or stringent cleanup standards. However, the size of the generated melt is limited. Because the technology is commonly used in situ, it may not be appropriate for sites where contaminated soil exists directly to buildings, other structures, or the property line (Li and Zhang 2013).

Dellisanti et al. (2009) demonstrated that the in-field scale Joule heating vitrification process is a suitable technology to remediate tons of soils contaminated by heavy metals. Based on Joule effect, the process led to the progressive heating and melting of the waste at high temperature. As a consequence of the cooling, the solidification and vitrification of the melted mass proceeded. The produced glassy monolith immobilized heavy metals. Leaching tests confirmed that the hazardous metals (Pb, Zn, and Zr) were immobilized within vitrified monolith, suggesting a high durability and leaching resistance of the glass to the chemical weathering.

Electrokinetic remediation

The electrokinetic method is a new remediation technology based on vitrification (Luo et al. 2004),

which is mainly the application of voltage at the two sides of soil to form an electric field gradient (FRTR 1999). It is suitable for low permeable soil, while being advantageous to easily install, operate, and undestroy the original natural environment at low cost (Alshawabkeh and Bricka 2013). Hence, it can achieve the environmental remediation and protect the original ecotype (Luo et al. 2004). However, direct electrokinetic remediation is incapable of controlling the pH value of soil system well, and the treatment efficiency is low. Electrokinetic remediation was also shown to be a time consuming process. Buried metal objects may be a big challenge to this type of remediation because the current flow will be diverted. Another limitation of electrokinetic remediation would arise, if non-targeted contaminants are present at high abundance (Ramalingam 2013).

Juris et al. (2015) investigated the efficiency of electrokinetic remediation for copper contaminated clayey soil (350 mg kg^{-1}) under laboratory conditions. Graphite electrodes (100 × 70 × 30 mm) were used through connection with non-copper wire to the power supply. The concentration of copper in water, when collected in the pockets (nearby the anode and cathode) after electrokinetic remediation of 40 days, was 0.05 and 0.085 mg L^{-1}, representing a negligible amount (around 0.02–0.03%) of the initial metal amount. This means that electro-osmosis was effective in draining the soil from water but unsuccessful in removing the heavy metals out from the soil.

In addition, Ottosen et al. (2012) indicated that the electrodialytic approach can be used for remediation of stationary, water saturated soils (in situ), or suspended soil (ex situ). In this regard, a direct comparison based on laboratory experiments was made for the two systems (suspended and stationary soils). In both experiments, Cu was removed most successfully at a removal rate of 77% for experiment suspended and 70% for stationary soils. In comparison, Pb exhibited a removal around 31% (Table 1).

Phytoremediation

Phytoremediation is the use of living green plants to fix or adsorb contaminants for cleaning the contaminants with the reduction of their risk. Phytostabilization, phytovolatilization, and phytoextraction are the main three types of phytoremediation (Shen and Chen 2000). The feasibility of the phytoremediation technology includes its aesthetically pleasing and passive approach, while relying on solar energy-driven technology. It can be applied to a variety of contaminants, while minimizing the generation of secondary wastes. It is cost-effective for large contaminated sites (with a low concentration of contaminants). The topsoil is left in a usable condition for agriculture. The soil can remain at the site after the removal of the contaminant rather than being disposed of or isolated. Phytoremediation treatment usually requires more than one growing season, which is one of the major disadvantages of this method. The treatment is limited to soils less than one meter from the surface and groundwater <3 m from the surface (Faisal et al. 2004). Climate and hydrologic conditions such as flooding and drought may restrict plant growth and the type of plants that can be utilized.

In general, hyperaccumulators are recommended for phytoremediation (Memon et al. 2001; Memon and Schröder 2009). Van der Ent et al. (2013), recommend the following concentration criteria for different metals and metalloids in dried foliage with plants growing in their natural habitats: (1) 100 mg kg^{-1} for Cd, Se and Tl; (2) 300 mg kg^{-1} for Co, Cu and Cr; (3) 1000 mg kg^{-1} for Ni, Pb and As; (4) 3000 mg kg^{-1} for Zn; 10,000 mg kg^{-1} for Mn. Generally, hyperaccumulators achieved 100-fold higher shoot metal concentration (without the reduction of yield) compared to crop plants or common nonaccumulator plants (Lasat 2002; Chaney et al. 2007). The Pteris vittata (Chinese brake fern) was illustrated to be resistant to As, with the high hyperaccumulating capability of As in its fronds (Ma et al. 2001), followed by adsorption by roots of plants. It is transported to their over ground parts to be removed via phytostabilization, phytoextraction, or phytovolatilization. The brake fern can accumulate between 1442 and 7526 mg kg^{-1} As in fronds from contaminated soils and up to 27,000 mg kg^{-1} As in its fronds in hydroponics culture.

Biological remediation

Bioremediation is a technology that uses microorganisms to treat contaminants through natural biodegradation mechanisms (intrinsic bioremediation) or through the enhancement of such capacity with the addition of microbes, nutrients, electron donors, and/ or electron acceptors (enhanced bioremediation) (EPA

2001). The microorganisms cannot degrade or destroy the heavy metals but can affect the migration and transformation by changing their physical and chemical characterizations. The remediation mechanisms include extracellular complexation, precipitation, oxidation–reduction reaction, and intracellular accumulation. The microbial leaching is a simple and effective technology for extracting valuable metals from low-grade ores and mineral concentrates. Besides the industrial application for raw materials supply, microbial leaching has potential for the remediation of mining sites, treatment of mineral industrial waste products, detoxification of sewage sludge, and for the remediation of soils and sediments contaminated with heavy metals (Bosecker 2001). The process is ecologically safe and natural, and is generally 60–70% less costly than other technologies. Bioremediation is vulnerable to variables such as temperatures, oxygen, moisture, and pH value. Its applications can also be limited to some microorganisms that can only degrade special contaminants. Also, the treatment time is typically longer than that of other remediation technologies (FAQs 2012).

Katsoyiannis and Zouboulis (2004) demonstrated that the microorganisms of Gallionella ferruginea and Leptothrix ochracea should support the biotic oxidation of iron. They performed some experiments in the laboratory where iron oxides and the above given microorganisms were deposited in the filter medium, offering a favorable condition for the adsorption of As. This is because As in the form of As(III) cannot be efficiently sorbed onto iron oxides. Probably, these microorganisms have oxidized As(III) to As(V), to facilitate the adsorption on Fe(III); as such, the overall removal efficiency of As went up to 95% even at high initial concentrations of As (200 mg L^{-1}).

Soil physicochemical reactions

Physicochemical properties of soils can change over the course of months and years in response to land use or management practice changes. These properties include organic matter, soil structure, infiltration rate, bulk density, and water- and nutrient-holding capacity. Changes in physicochemical or in other words dynamic properties of soils depend both on land management practices and the inherent properties of the soil. For example, the organic matter (OM) levels

in soil generally depend on the combined effects of tillage practices and the types of plants growing (management). However, the total amount of OM is constrained by soil texture and climate (inherent features). Metal(loid) ions can be retained in the soil by sorption, precipitation, and complexation reactions.

Sorption and desorption process

The mobility and availability of heavy metals are controlled by the sorption and desorption characteristics of soil. The adsorption and desorption of metals have been correlated with such soil properties as pH, redox potential, clay minerals, soil organic and inorganic matter, Fe and Mn oxides, and $CaCO_3$ content (McLean and Bledsoe 1992). Hence, the basic information regarding the capacity of soils to retain and release metals is essential to predict the environmental impact on the use of residues such as sewage sludge containing heavy metals (Silveira et al. 2003).

The effect of inorganic anions on the sorption of metal(loid) cations such as Pb and Cd was explained by two different mechanisms (Hong et al. 2008). According to Hong et al. (2008), inorganic anions are likely to form ion pair complexes with metal(loid)s, thereby reducing their sorption. Naidu et al. (1997) supposed that the specific sorption of ligand anions is likely to increase the negative charge on soil particles, thereby increasing the sorption of Cd. With increasing pH, soil organic matters of several functional groups (carboxyl, phenolic, alcoholic, and carbonyl) should dissociate, thereby increasing the affinity of ligand ions for these metal(loid) cations. The extent of metal(loid)–organic complex formation, however, varies with a number of factors including temperature, steric factors, and concentration (Bolan et al. 2014).

When the concentration (or pressure) of a substance in the bulk phase is lowered, some of the sorbed substance changes to the bulk state which called desorption (Silveira et al. 2003). The more a chemical desorbs, the less likely it will adsorb. This gives an idea of the strength of the association of the metal with the soil surface.

Precipitation and dissolution

Precipitation and dissolution can play an important role in soil immobilization. Precipitation/dissolution is a significant process to modify the physical and

chemical properties of fractured media. Physical changes of properties (fracture aperture, tortuosity, effective mass diffusivities, and permeabilities) are coupled with such variables affecting the subsequent fluid flow, solute transport, and the precipitation/dissolution reactions (Dijk and Berkowitz 1998). In a closed system, the amount and composition of a mineral that dissolves or precipitates may be described in terms of chemical thermodynamics and kinetics as affected by the surface morphologies of the dissolving and precipitating species (Ritchie 1994).

Precipitation appears to be the predominant process in high pH soils and in the presence of anions (such as SO_4^{2-}, CO_3^{2-}, OH^-, and HPO_4^{2-}), when the concentration of the heavy metal(loid) ion is high (Hong et al. 2007; Ok et al. 2011). Precipitation of metal(loid) phosphates/carbonates is considered a mechanism for the immobilization of heavy metal(loid)s such as Cu and Pb, especially in substrates containing high concentrations of these metal(loid)s. For example, McGowen et al. (2001) observed that phosphorous decreased the leaching of Cd, Pb, and Zn.

As many ionic compounds are applied to dissolve in water to form aqueous solutions through dissociation, an ionic compound is separated into its component ions. When surface reactions are fast relative to molecular diffusion, dissolved species are depleted at the solid surface; the reaction is thus "transport" controlled. If transport is fast relative to surface reactions, no depletion is observed; the overall reaction rate is controlled by "surface reaction" (Schott et al. 2009).

Oxidation and reduction of soil heavy metals

Redox reactions can be important in altering the mobility and toxicity of inorganic contaminants. This principle can be used to remediate various types of metal contaminants. The oxidation or reduction of metals may be performed directly by the organism or may be a result of a reducing agent produced by the organism. An increase in mobility is one of the outcomes of microbial oxidation (or reduction) of metals that can be exploited for remedial purposes (McLean and Bledsoe 1992). The redox potential of a soil system can also be defined by the measure of the electrochemical potential or availability of electrons within a system.

Metal(loid)s, including As, Cr, Hg, and Se, are subject to microbial redox reactions through which their speciation and mobility are influenced (Table 2). For example, metals (e.g., Cu and Hg) generally are less soluble in their higher oxidation state. In addition, the solubility and mobility of metalloids (e.g., As) depend on both the oxidation state and the ionic form (Whitacre 2013).

Chromate (Cr(VI)) can be reduced to Cr(III) in environments where a ready source of electrons (Fe(II)) is available and microbial Cr(VI) reduction occurs in the presence of OM as an electron donor (Hsu et al. 2009; Choppala et al. 2012). The bioreduction of selenate, the most labile and highly toxic inorganic form of Se through redox reactions was seen to result in lowering of Se, levels in soils and aquatic environment. Reduction reaction has been more successfully employed for the bioremediation of contaminated waters (Iskandar 2001). In living systems, Se tends to be reduced rather effectively than oxidized, while such reduction occurs under both aerobic and anaerobic conditions. Se(IV) reduction to Se(0) by chemical reductants (such as sulfide or hydroxylamine, or biochemically by glutathione reductase) is the major biological transformation for remediation of Se oxyanions in anoxic sediments (Zhang and Frankenberger 2003).

The use of soil amendments for site remediation

Among various remediation technologies, in situ immobilization of heavy metals using a chemical amendment can be considered as a cost-effective and environmentally sustainable remediation approach by reducing the mobility and availability of metals (Vangronsveld et al. 1996). Stabilization/solidification is best suited for soils contaminated with metals, radionuclides, other inorganic compounds, and non- or semi-volatile organic compounds. USEPA has identified S/S as the best demonstrated available technology (BDAT) for 57 types of hazardous wastes listed in RCRA (Means 1995). About 25% of the Superfund remediation sites were treated by S/S technologies compared to other technologies in the USA (USEPA 2012). To date, many types of materials including lime (Geebelen et al. 2003; Gray et al. 2003), organic matter (Brown et al. 2004), calcium carbonate (Houben et al. 2012) red mud (Lee et al. 2009), bone

Table 2 Effect of various soil amendments on the redox reactions of metal(loid)s in soils

Metal(loid)s	Soil amendments	Observations	References
As	Iron oxide	At lower redox, insoluble sulfides can be formed either with iron (FeAsS, arsenopyrite; at strongly reducing conditions) or without iron (As_2S_3, orpiment; at moderately reducing conditions)	Porter et al. (2004)
As	Fe(III) and Mn(III) oxides	Fe(III) and Mn(III) oxides oxidized As(III) to As(V) through electron transfer reaction	Mahimairaj et al. (2005)
Cr	Zero valent iron (ZVI)	Enhanced the reduction of Cr(VI) to Cr(III)	Kumpiene (2010)
Cd	MW-H_2O_2 (Microwave-assisted hydrogen peroxide)	Release efficiency of Cd when pH went higher than 4 declined dramatically (followed by oxidation reaction)	Wang et al. (2014)
Cd	LS (limestone + sepiolite) and HZ (hydroxyhistidine + zeolite)	Significant increase in soil pH values and CEC, and obvious decrease in solubility and mobility of oxidized Cd metals and reduced it	Zhou et al. (2014)
Cu	MW-H_2O_2	Release efficiency of Cu was stable with pH varying from 0 to 4 and increased with increasing pH (followed by oxidation reaction)	Wang et al. (2014)
Cu	LS (limestone + sepiolite) and HZ (hydroxyhistidine + zeolite)	Reduced the bioavailability of oxidized Cu, and significantly decreased the uptake and accumulation of Cu in rice tissues	Zhou et al. (2014)
Pb	MW-H_2O_2	The release efficiency of Pb increased significantly with increasing temperature, while after treatment Pb had more stability in the sediment and lower risk to the environment	Wang et al. (2014)
Pb	LS (limestone + sepiolite) and HZ (hydroxyhistidine + zeolite)	Inhibited uptake and accumulation of Pb in rice plants followed by redox reaction in soil	Zhou et al. (2014)
Zn	MW-H_2O_2	The oxidization rate of metal sulfides and the degradation rate of metal-bound organic compounds would increase correspondingly, and the release of Zn would be accelerated	Wang et al. (2014)
Zn	LS (limestone + sepiolite) and HZ (hydroxyhistidine + zeolite)	Using LS and HZ oxidized Zn, thus reduced Zn bioavailability and accumulation in rice grown on polluted soils	Zhou et al. (2014)
Hg	Green rust (mixture of Fe^{II}/Fe^{III} hydroxides)	Reduced Hg(II) to Hg(0) in suboxic soils and sediments	O'Loughlin et al. (2003)
Se	Green rust	In suboxic conditions, green rust reduced Se(VI) to Se(0)	Myneni et al. (1997) and Refait et al. (2000)
Se	Zero valent iron	Reduced Se(VI) to insoluble selenide (Se(-II)) species	Olegario et al. (2010)

meal (Houben et al. 2012; Lee et al. 2009; Sneddon et al. 2006), and fly ash (Houben et al. 2012) were used to the media for soil amendments. The addition of the different amendments did not change the main chemical properties of the polluted soil with some exceptions (pH, electrical conductivity, and exchangeable Na and K). Therefore, soil amendments resulted in the redistribution of contaminants from solution phase to solid phase, thereby reduced their bioavailability and transport in the environment (Porter et al. 2004). In this section, some of the promising soil amendments are reviewed and the potential value of these soil amendments through the immobilization of metal(loid)s is discussed in relation to remediation materials.

Liming compounds

Lime (e.g., $CaCO_3$, CaO, $Ca(OH)_2$) is a calcium-containing inorganic material in which carbonates, oxides, and hydroxides are predominant. Lime stabilization treatment of contaminated soils laden with hazardous waste (e.g., acid mining disposal) is proven as a reliable

technology. Both the technology and its acceptance have progressed dramatically over the years. It is a simple, cost-effective, flexible treatment method for remediation of soils and recycling them back to usable land (USDA 1999).

Although liming is primarily aimed at ameliorating soil acidity, it is increasingly employed as an important management tool in reducing the toxicity of heavy metal(loid)s in soils (Table 3). Lime can increase the negative charge in soils subsequently precipitate metals as hydroxides. Calcium released from lime followed by plant absorption could inhibit the translocation of metals specially Cd, Cu, Pb, and Zn from roots to shoots (Hakeem et al. 2014; Zhou et al. 2014). However, there are limitations associated with lime treatment of contaminated soils. Agricultural limestone has low solubility and can become coated and ineffective at severely acidic soils. In addition, it can be source of fugitive dust and may increase soil pH as high as not to be appropriate for optimum plant growth if in high ratio added in soil (EPA 2007).

As a consequence, it is common practice to apply liming materials to treat problems associated with soil acidity (Wong 2003), or alternatively to apply lime-stabilized biosolids (Adriano et al. 2004). Several authors demonstrated that the application of biosolids in combination with alkaline residues to severely metal-contaminated soils is sufficient to restore a vegetative cover (Brown et al. 2005).

Metal oxides

Oxides of metals (such as Fe, Al, Ti, and Mn) play an important role in soil metal(loid) geochemistry. Metal oxides can strongly bind metal(loid)s through specific sorption, co-precipitation, and by forming inner sphere complexes. Naturally occurring oxides, synthesized oxide particles, as well as industrial by-products, have been studied for their suitability to be used for soil remediation purposes (Appelo and Postma 2005; Kumpiene et al. 2006). The surface charge of a metal (M) oxide is thus the sum of positively and negatively charged sites resulting from its amphoteric character (Dzombak and Morel 1990):

$$=MOH_2^+ \rightarrow MOH^0 + H^+ \qquad (1)$$

$$=MOH^0 \rightarrow =MO^- + H^+ \qquad (2)$$

The distance between the OH–OH groups in the Fe, Mn, Al oxides matches with the coordination polyhedra of many metal(loid) cations and anions, which are adsorbed on different surface sites, the former share edges and the latter double corners with $Fe(O,OH)_6$ octahedra (Manceau et al. 1992). The presence of organic and inorganic ligands in soils and their complexation with the metal(loid)s significantly influences their adsorption onto oxides and thus affects the stabilization efficiency (Zaman et al. 2009; Zhu et al. 2011a, b).

Among the available adsorbents, nanosized metal oxides (NMOs), including nanosized ferric oxides, manganese oxides, aluminum oxides, titanium oxides, magnesium oxides, and cerium oxides, have great potentials to remove heavy metals such as As, Cd, Cu, Pb, and Zn from the environment because of large surface areas and high activities (Agrawal and Sahu 2006; Hua et al. 2012). Because elemental iron is environmentally friendly, NFeOs (nanosized iron oxides) can be used directly to contaminated sites with a negligible risk of secondary contamination (Deliyanni et al. 2004). The nanosized iron oxides (NFeOs) were intensively studied for heavy metals removal from water/wastewater. They include goethite (–FeOOH), hematite (–Fe_2O_3) (Chen et al. 1997a, b), amorphous hydrous Fe oxides (Fan et al. 2005), maghemite (–Fe_2O_3) (Hu et al. 2005, 2006), magnetite (Fe_3O_4) (Wang et al. 2010; Badruddoza et al. 2011), and iron/iron oxide (Fe/Fe_xO_y) (Macdonald and Veinot 2008). For instance, Marsz (2014) evaluated iron oxide (ZVI) on As, Cu, Pb, and Ni solubility in contaminated soils after 16 and 6 years applying treatments. Results demonstrated that ZVI addition could be a suitable amendment to immobilize As and Cu for a long time. However, Cu was significantly pH dependent. As some of metal oxides (e.g., steel slag) include high content of Zn and volatilize ammonia, their application may cause problems (EPA 2007).

Phosphate compounds

A phosphate (PO_4^{3-}) as an inorganic chemical is a salt of phosphoric acid. A large number of studies have provided conclusive evidence for the potential value of both water-soluble (e.g., DAP "diammonium phosphate") and water-insoluble (e.g., apatite, also

Table 3 Overview of soil amendments feasibility in the immobilization of metal(loid)s in contaminated soils

Amendments	Metal(loid)s	Observations	References
Liming materials			
Fe(II)-modified Zeolite (Fe-Z), Zero valent iron (ZVI) and soluble Fe(II)	As	The immobilization of As(III) with Fe(II), ZVI, and Fe-Z was 90.6, 92, and 81.4%, respectively	Naseri et al. (2014)
Single superphosphate, calcium magnesium phosphate and phosphate rock	Pb	Decreased the availability and uptake of Pb by 29–9%, respectively	Tang et al. (2014)
Limestone + sepiolite, hydroxyhistidine + zeolite	Pb, Cd, Cu, Zn	Concentrations of Pb, Cd, Cu, and Zn in brown rice were decreased by 31.8–16.3%, respectively, as a result of 0.8% addition of LS, and by 40.8–21.7%, respectively, as a result of 0.8% addition of HZ	Zhou et al. (2014)
Lime	Pb, Zn, Cu, As	Pb increased 6%, but Cu, Zn, and As concentrations decreased 20–2%, respectively. Thus, the bioavailable concentrations of heavy metals remarkably decreased except Pb	Bade et al. (2012)
Hydrated lime	Cd, Co, Cu, Ni, Pb, Sb, and Zn	Reduced concentration of every trace element almost 100% in leachate at pH 7–8.5, except Sb	Hale et al. (2012)
Red mud, natural zeolite, lime	Pb, Cd, Zn	Red mud was the most efficient treatment able to retain Pb and Cd. The efficiency in the treated soil was 52 and 83%, respectively	Garau et al. (2007)
$Ca(OH)_2$	Cd	Transformed to less mobile fractions, reduced phytoavailability	Bolan et al. (2003)
Dolomite	Cd, Cu, Pb	Reduced the concentration of Cd, Cu and Pb by 97, 80, and 73%, respectively	Illera et al. (2004)
Zeolite, compost, calcium hydroxide	Zn, Cd, Pb	Increased residual fraction of Zn, Cd, and Pb in soils using Zeolite, compost, calcium hydroxide by 80, 55%, and 45, 78, 37%, and 46, 77, 47%, and 53%, respectively	Castaldi et al. (2005)
Metal oxides			
Penghu soil (PHS), Mn oxide(MO) + PHS	Cd, Pb	Using PHS and MO + PHS reduced uptake of metals by Chinese cabbage about 77.3 and 75% for Cd and 89.6 and 87.9% for Pb, respectively	Cheng and Hseu (2002)
Amorphous manganese oxide (AMO)	Cu, As, Pb, Sb, Cd, Zn	No effect on leaching of Cd and Zn after AMO treatments, while the leaching of Cu, As, Pb, and Sb decreased by 35–11% of the control	Ettler et al. (2015)
Fe-rich waste (FeW), FeW + organic waste (OW)	Cd, Cu, Pb, Zn	Exchangeable Zn was reduced in the FeW + OW treated soil by 90%. DTPA-extractable Cd, Cu and Zn were decreased significantly after one to three redox cycles by 98–36%	Contin et al. (2007)
Geothite, iron grit, iron(II) and (III)	As	Reduced transfer coefficients of As in spinach shoots by 100–80%	Hartley and Lepp (2008)
Phosphate compounds			
Bonemeal (finely ground, poorly crystalline apatite)	Zn, Cd, Ni, Pb	Reduced metal(loid) concentration in the leachate from soil columns about 66–14%	Hodson et al. (2000)
KH_2PO_2	Cd, Zn, Pb	Reduced the solubility and bioavailability of Pb within the soil, not Cd and Zn	Pearson et al. (2000)

Table 3 continued

Amendments	Metal(loid)s	Observations	References
Phosphate rock, diammonium phosphate (DAP)	Cd, Pb, Zn	Rock phosphate reduced Pb, Cd, and Zn by 99.9–24%, DAP reduced Cd and Zn by >77% and >91% for Cd	Basta and McGowen (2004)
Phosphate rock	Cd, Pb, Zn	Phosphate rock of the smallest grain size (<35 μm) reduced uptake in plant (*Brassica oleracea* L.) shoots for Cd, Pb, and Zn, by 50.0–34.6%	Chen et al. (2006)
Organic matter and biochar			
Organic matter	Ni, Cd, Zn	The overall reduction of metal concentration was 89–21% for Cd, Ni, and Zn	Kashem and Singh (2001)
Organic matter	Cd	Decrease Cd bioavailability, since Cd concentration in the nutrient solution without plants decreased 20% in the presence (vs. absence) of OM	Pinto et al. (2004)
Compost (C), compost + cyclonic ashes (C + CA), compost + cyclonic ashes + steel shots (C + CA + SS)	Cd, Cu, pb, Zn	Strongest reductions occurred after CA + SS and C + CA + SS treatments (99–97% for Cd and Zn), while Pb and Cu leaching increased after C and C + CA treatment (3.3–17%, respectively)	Ruttens et al. (2006)
Hard wood biochar	Cd, Zn	Increased immobilization of Cd and Zn about 65–11% (due to enhanced pH), respectively	Beesley et al. (2010)
Biochar soil amendment	Cd, Pb	Extractable Pb and Cd in the rice field were significantly reduced by 79.6–70.9% throughout the two and one year, respectively	Bian et al. (2014)
Chicken manure and green waste biochars	Cd, Cu, Pb	Extractable Cd and Pd contents were decreased by 88 and 94%, respectively	Park et al. (2002)
Goethite, iron grit, iron(II) and (III) sulfate	As, Cu, Zn	Reduced plant shoot As, Cu, and Zn content by 99.5–98%, respectively	Hartley and Lepp (2008)

known as PRs "phosphate rocks") phosphorous (P) compounds to immobilize metals in soils. As such, their bioavailability for plant uptake can also be limited at the same time. It is, however, important to recognize that, depending on the nature of P compounds and the heavy metal species, application of these materials can cause either mobilization or immobilization of the metals. Furthermore, as some of these materials contain high levels of metals, they can act as a transport agent of metal to soils. Accordingly, these materials should be scrutinized before their large-scale use as immobilizing agent in contaminated sites.

Phosphate compounds enhance the immobilization of metal(loid)s such as Cd, Pb, and Zn in soils through various processes including direct metal(loid) adsorption/substitution by P compounds, P anion-induced metal(loid) adsorption, and precipitation of metal(loid)s with solution P as metal(loid) phosphates.

Precipitation as metal(loid)–P has proven to be one of the main mechanisms for the immobilization of metals such as Pb and Zn in soils (Table 3). Because these fairly stable metal–P compounds have extremely low solubility over a wide pH range, the P application is considered an attractive technology for managing metal(loid)-contaminated soils (Chen and Li 2010).

Experiments involving the treatment of metal contaminated soils with rock phosphates (apatite and hydroxyapatite) confirmed that the formation of metal phosphate causes to precipitate heavy metals followed by reduction in their solubility. Insoluble and geochemically stable lead pyromorphites such as hydroxypyromorphite $[Pb_5(PO_4)_3OH]$ and chloropyromorphite $[Pb_5(PO_4)_3Cl]$ have been found to control Pb solubility in apatite amended contaminated soils (Ma and Rao 1997; Chen and Li 2010). The efficiency of P-induced metal(loid) immobilization in soil can be enhanced by increasing the solubility of P compounds. In addition,

the co-application of phosphoric acid and rock phosphate effectively immobilized Pb and Zn (Cao et al. 2009). Phosphate solubilizing bacteria were employed to increase Pb immobilization in soil by slowly releasing P from insoluble P rock (Park et al. 2010, 2011). As the large-scale use of P compounds can contaminate surface and groundwater, future research should aim to develop the remediation method with the minimum impact of P on quality of water sources (Bolan et al. 2003).

Biochar

Biochar is a porous, carbonaceous product obtained from the pyrolysis of organic materials. Numerous materials can be used as feedstocks, including sludges, plant materials, and manures. Although the use of charcoal (wood biochar) has been common since preterit times, the idea of using other feedstocks for biochar production is new and relatively unexplored. Typically, biochars have high cation exchange capacity and are alkaline. Biochar has many potential benefits on soil properties with an increase in soil biological activity (Lehmann et al. 2011; Paz-Ferreiro and Fu 2014), diminishing soil greenhouse gas emissions from agricultural sources and thus enhancing soil carbon sequestration due to its elevated content of recalcitrant forms of carbon (Gascó et al. 2012).

One of the characteristics of biochars is large surface areas, with a high capacity for heavy metals uptake. Surface sorption of heavy metals on biochar has been demonstrated on multiple occasions using scanning electron microscopy (Beesley and Marmiroli 2011; Lu et al. 2012). This sorption can be due to the complexation of the heavy metals with different functional groups (e.g., O-alkylated carbons and anomeric O–C–O carbons as well as fused-ring aromatic structures and aromatic C–O groups which define pH and electrical conductivity in derived biochar) present in the biochar (Uchimiya et al. 2011) (Table 3). The exchange of heavy metals proceeds with cations associated with biochar, such as Ca and Mg (Lu et al. 2012), K, Na and S (Uchimiya et al. 2011), or due to physical adsorption (Lu et al. 2012). Alkalinity of biochar can also be partially responsible for the lower concentrations of heavy metals in biochar-amended soils. Biochar pH values were found to increase with pyrolysis temperature (Wu et al. 2012), which was associated with a higher

proportion of ash content (Cantrell et al. 2012). Biochar can also reduce the mobility of heavy metals, altering their redox state. Indeed, biochar is a reductant, but its electrochemical properties are dependent of the temperature and the concentration of the various redox active minerals. Hence, when biochars are added to soils, they interact with plant roots, soil organic matter and microorganisms to form organo-mineral–biochar complexes (Joseph et al. 2015).

Uchimiya et al. (2010) suggested that biochar application can increase the soil pH and cation exchange capacity and subsequently enhance the immobilization of heavy metals in soil. Ahmad et al. (2012) used mussel shell, cow bone, and biochar to reduce Pb toxicity in the highly contaminated military shooting range soil in Korea. Bioavailability of Pb in the soils was found to decrease by 75.8% with biochar treatment. However, it is known that a large problem with biochar is the lack of supply and variable quality of the product (Embren 2016).

Organic matter (OM)

Soil OM is one of the important factors governing uptake of soil metal species by plants, and transition metal cations tend to form stable complexes with organic ligands (Elliot et al. 1986). As OM can form strong complexes with heavy metals, its content can affect the speciation of heavy metals in soil (Koretsky 2000). Humic substances such as humic acid (HA) and fulvic acid (FA) come from the decomposition of plant and animal residues. Complexation by HA is of great interest in environmental studies, as the interaction of these ligands with heavy metals determines their bioavailability, toxicity, and mobility to a large extent (Giannis et al. 2007). Cationic, anionic, and nonionic surfactants are used to increase the treatment efficiency of heavy metals (e.g., Ni, Cd, and Zn) as they can help reduce the mobility of metals in the soil layer.

The enrichment of OM in soil could reduce the content of bioavailable metal species due to complexation of metal free ions (Skáodowski et al. 2006). In line with this principle, high OM content was reported to decrease Cd and Ni in soil solution (Arnesen and Singh 1999) (Table 3). The application of brown coal preparations as a source of OM is a well-known practice to improve soil properties (e.g., enrichment of humic acids molecules in carbon and nitrogen) because of its sufficiently slow mineralization

(Kwiatkowska et al. 2005). This is very important because a high content of OM in contaminated soil is one simple reason to exclude heavy metals from the trophic chain (Kwiatkowska et al. 2005). Maity et al. (2013) demonstrated that the use of a biodegradable natural plant-based surfactant extracted from soapberry is promising for the remediation of Ni, Cr, and Mn from industrial soil site in Hai-Pu, Taiwan. Noteworthy, if too many OM is added into soil, nutrition can be released at the short time, an outflow of them into the groundwater and subsequently make water polluted. In addition, the incorporation of OM in soil can be time consuming.
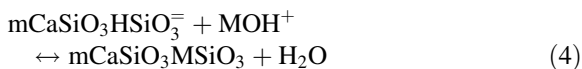
Soil stabilization mechanisms

There are several processes that govern metal retention in soil. Overall, the reaction of a metal (M) with a SiO_2 substrate which is existed in some of organic/inorganic soil amendments may result in the formation of both metal silicides and metal oxides, i.e., $M_x + SiO_2 \rightarrow M_y - Si + M_{x-y}O_2$. Silicon dioxide (silica) is one of the most commonly encountered substances in metal stabilization. Metal adsorption ions through SiO_2 bond may also involve different silica in biochar as shown below (Ricou-Hoeffer et al. 2000).

In acid solutions,

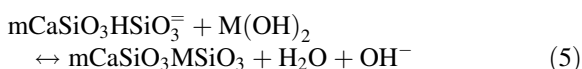$$SiOH\cdots H-O-H\left[M(OH_2)_3\right]^{2+} \leftrightarrow Si-OM + H_3O^+ \tag{3}$$
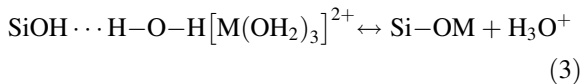
Amendments with high CaO contents are thought to have higher adsorption efficiency due to the formation of Ca and Si complexes such as calcium silicates ($2CaO * SiO_2$).

In neutral solutions,

$$mCaSiO_3HSiO_3^= + MOH^+ \\ \leftrightarrow mCaSiO_3MSiO_3 + H_2O \tag{4}$$

In alkaline solutions,

$$mCaSiO_3HSiO_3^= + M(OH)_2 \\ \leftrightarrow mCaSiO_3MSiO_3 + H_2O + OH^- \tag{5}$$

In general, metals exist in soil solutions as free metal ions, in soluble complexes with inorganic and organic ligands or associated with organic/inorganic colloidal material (Shuman 1991). The calcite in soil can react with heavy metals to form surface precipitation on soil, which can be explained by:
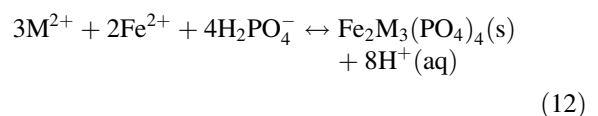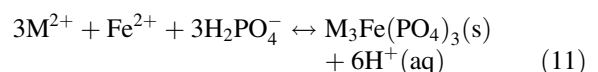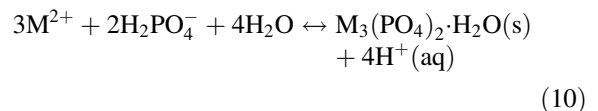
$$M^+ + H_2O \rightarrow M(OH)^+ + H^+ \tag{6}$$

$$M(OH)^+ + CaCO_3(s) \rightarrow MCO_3(s) + Ca^{2+} + OH^- \tag{7}$$
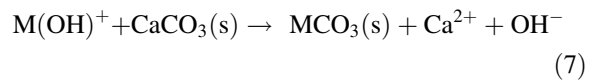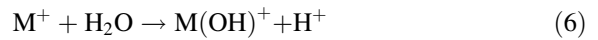
In addition, the mechanism of heavy metal stabilization by chemical precipitation in amendments which include (OH^-) is presented in Eq. (8) (Wang et al. 2005):
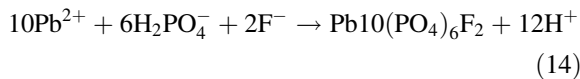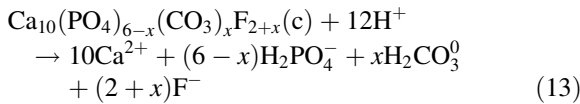
$$M^{2+} + 2OH^- \rightarrow M(OH)_2(s) \tag{8}$$
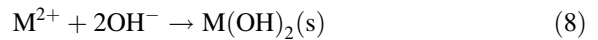
Therefore, metals can precipitate as pure solids; MCO_3, $M(OH)_2$, MS_2, or co-precipitate producing mixed solids, e.g., $(Fe_x,Cr_{1-x})(OH)_3$ or the occurrence of solid formation when metals are compatible with the host elements and can replace them throughout the mineral, for example, substituting with Ca in $CaCO_3$.
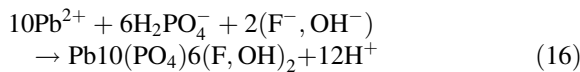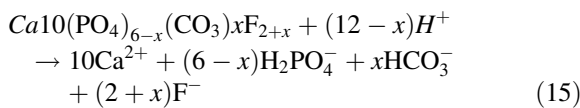
The relative amounts of the three phosphate species ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) are governed by the pH of the ambient condition. Two ionic forms of $H_2PO_4^-$, HPO_4^{2-} are known as the most important species in agricultural soils due to be formed at pH values of 2 and 7, respectively. As the pH increases, the concentration of divalent HPO_4^{2-} ion increases tenfold for each unit in pH (Lindsay 1979). Generally, solubility of phosphate increases with increasing pH above 4, while phosphate adsorption increases at the lowest pH. Both phosphate-containing minerals and soluble phosphate have been advocated as sources of PO_4^{3-} which are important to sorb metals at their surfaces. The major reaction in case of phosphate minerals treated soils at the slightly acidic pH condition is believed to be as follows:

$$3M^{2+} + 2H_2PO_4^- \leftrightarrow M_3(PO_4)_2(s) \tag{9}$$

$$3M^{2+} + 2H_2PO_4^- + 4H_2O \leftrightarrow M_3(PO_4)_2 \cdot H_2O(s) \\ + 4H^+(aq) \tag{10}$$

$$3M^{2+} + Fe^{2+} + 3H_2PO_4^- \leftrightarrow M_3Fe(PO_4)_3(s) \\ + 6H^+(aq) \tag{11}$$

$$3M^{2+} + 2Fe^{2+} + 4H_2PO_4^- \leftrightarrow Fe_2M_3(PO_4)_4(s) \\ + 8H^+(aq) \tag{12}$$

At neutral to high pH, phosphate reacts with calcium to form minerals such as apatites. Indeed, apatites are the principal mineral component of phosphate rock. It has been explored that apatites [e.g., calcium hydroxyapatite, $Ca_5(PO_4)_3OH$] or waste phosphate rock as a source to precipitate metals, such as Pb^{2+} in contaminated soils as lead hydroxypyromorphite ($Pb_5(PO_4)_3OH$); a more thermodynamically stable isostructural analogue to calcium hydroxyapatite (Laperche et al. 1996). In the case of soluble phosphate, chemical stabilization mechanisms can involve a continuum from surface sorption processes to existing or newly formed particulate surfaces in a waste material, through the formation of new surface precipitates, to the formation of discrete heterogeneous or homogeneous precipitates (Nriagu 1974). The reaction of mineral apatite with heavy metals is complicated because of the coexistence of PO_4^{3-}, CO_3^{2-}, F^-, OH^-, and other cations in the structure of mineral apatites. Chen et al. (1997a, b) demonstrated at the acidic pH (<6), the carbonates dissolved from apetite, and thus, the activities of carbonate and OH^- ions were extremely low (Eqs. 13, 14).

$$Ca_{10}(PO_4)_{6-x}(CO_3)_xF_{2+x}(c) + 12H^+$$
$$\rightarrow 10Ca^{2+} + (6-x)H_2PO_4^- + xH_2CO_3^0$$
$$+ (2+x)F^- \quad (13)$$

$$10Pb^{2+} + 6H_2PO_4^- + 2F^- \rightarrow Pb10(PO_4)_6F_2 + 12H^+ \quad (14)$$

While at the neutral pH an increase in the activity of OH^- and the formation of hydroxyl fluoropyromophite resulted reactions as below:

$$Ca10(PO_4)_{6-x}(CO_3)xF_{2+x} + (12-x)H^+$$
$$\rightarrow 10Ca^{2+} + (6-x)H_2PO_4^- + xHCO_3^-$$
$$+ (2+x)F^- \quad (15)$$

$$10Pb^{2+} + 6H_2PO_4^- + 2(F^-, OH^-)$$
$$\rightarrow Pb10(PO_4)6(F, OH)_2 + 12H^+ \quad (16)$$

The solubility of apatites is highly pH dependent with lower solubility at higher pH (Kanabo and Gilkes 1987), which resulted in a drop of dissolved phosphate, carbonate, and fluoride, and subsequently precipitation of Pb.

Specific adsorption can be described by a surface complexation model which defines surface complexation formation as a reaction between functional surface groups and an ion in a surrounding solution, which form a stable unit (Schindler et al. 1976). Specific adsorption is based upon adsorption reactions at OH groups at the soil surfaces and edges, which are negatively charged at high pH. The adsorbing cation bonds directly by an inner sphere mechanism to atoms at the surface. As a consequence, the properties of the surface and the nature of the metal constituting the adsorption site influence the tendency for adsorption. These reactions depend largely on pH, are equivalent to heavy metal ion hydrolysis, and can be described as follows for a metal cation M and a surface Sc:

$$Sc-OH + M^{2+} + H_2O \leftrightarrow Sc-O-MOH_2^+ + H^+ \quad (17)$$
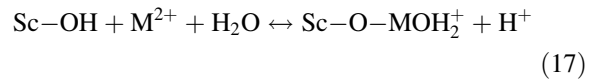
In contrast to adsorption, surface precipitation is characterized by the growth of a new solid phase, which repeats itself in three dimensions (Sposito 1984). The surface precipitation model can be described by two reactions: first a surface complex formation of a metal cation and a surface as described by Eq. (18) and second the precipitation of M at the surface Sc:

$$Sc-O-MOH_2^+ + M^{2+} + H_2O$$
$$\leftrightarrow Sc-O-MOH_2^+ + M(OH)_2(s) + 2H^+ \quad (18)$$
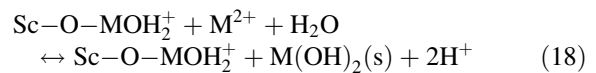
Generally, metals have been shown to be able to absorb onto organic matter, clay minerals, iron and manganese oxides and hydroxides, calcium carbonates and amorphous aluminosilicates, the organic matter in this case consisting of biochemicals and humic substances. They provide acid functional groups, carboxylic, phenolic, alcoholic, and amino groups as adsorption sites. These are the main reactions that can be considered between soil amendments and soil metals.

Comparison among efficiency of remediation technologies

Pollution associated with agricultural activities is a global issue for the preservation of water, air, and land resources. Impurities such as trace elements, fluoride, and total dissolved salts commonly contained in used industrial wastes could easily be leached through soil to groundwater and/or exported through runoff to receiving water to spread pollution into the

environment. The remediation technologies based on screening matrix are a user-friendly tool to screen for technologies for a remediation project. The matrix allows you to screen through in situ and ex situ technologies for either soil or groundwater remediation. Key variables for screening include contaminants, development status, overall cost, and cleanup time. The key criteria for screening technologies are presented in Table 4 (EPA 2002). Both specific site and contaminant characteristics may limit the applicability and effectiveness of any of the technologies and treatments listed below. This matrix is optimistic in nature and should always be used in conjunction with the referenced text sections, which should contain additional information that can be useful in identifying potentially applicable technologies. Referring to this screening matrix table, the efficiency of each method is indicated by a number from 1 to 3; the smaller the ratio, the higher efficiency is.

Many techniques have been devised over the past few decades to remediate heavy metal contaminated soil. In this review, the utilization of different soil remediation technologies for different heavy metals was evaluated in terms of treatment efficiency

(Table 5). There are generally two major strategies to improve the quality of the soil: removal of heavy metals and their irreversible immobilization. Based on the comparison results reported in Table 4, the most cost-effective and applicable strategy of remediation is the irreversible immobilization of heavy metals as the lowest score for sum of A (obtained from Table 3) + B (obtained from Table 5) was observed for this method. Hence, the in situ immobilization low heavy metal(loid) content and reduced metals bioavailability may offer a promising option. In this approach, the risks related to the presence of soluble or available heavy metal ions are reduced, although the metals are still present. However, they are converted into an insoluble state to reduce the risk of leaching from the ground, while making them available for further bioremediation.

Summary and conclusions

Soil is a very unique part of the natural and agricultural aspects of the terrestrial ecosystem, given its role in the growth of plants and the degradation and recycling

Table 4 Screening matrix for treatment technologies (EPA 2002)

Remediation technologies for heavy metals	Evaluation for remediation technologies							
	Development status	Treatment train	Relative cost	System reliability and maintainability	Time	Availability	O&M	Sum (A)
Physical remediation								
Soil replacement	1	1	$-^a$	1	1	1	1	8–10
Soil spading	1	2	2	2	2	1	2	14
New soil importing	1	2	1	1	3	1	2	12
Thermal desorption method	1	1	2	2	1	1	3	13
Soil washing	1	3	2	1	1	1	3	14
Chemical remediation								
Solidification/stabilization	1	1	1	1	1	1	2	10
Vitrification	1	1	1	1	2	1	3	13
Electrokinetic	1	3	3	2	2	2	3	18
Phytoremediation								
Phytostabilization/phytoextraction	1	1	1	3	3	2	1	13
Biological remediation								
Enhanced bioremediation	2	1	1	2	2	1	3	13

1—Excellent (80–100% removal), 2—Acceptable (50–80% removal), 3—Unsatisfactory (<50% removal)

O&M operation and maintenance intensive

[a] Not detected

Table 5 Heavy metals removal efficiency using different remediation technologies

Remediation technologies	Removal efficiency									Sum (B)	Sum (A + B)	References
	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Zn			
Physical remediation	1	1	1	3	1	1	1	–[a]	3	12	24–25	Li et al. (2010), Kumpiene et al. (2009), Zhang et al. (2014), Yu-Ling (2012), Nordmark et al. (2011), Cocârt et al. (2013) and EPA (1991)
Soil washing (chemical washing)	1–2	1	3	2	3	2	2	3	1–2	18–20	32–34	Hseu et al. (2014), EPA (2002) and Yao et al. (2012)
Solidification/stabilization	1	1	1	1	1	1	1	2	1	10	20	Makino et al. (2007), Frankenberger and Arshad (2001), Abdelhafez et al. (2014), Devasena and Nambi (2013), Dermatas and Meng (2003), Hytiris et al. (2015), Moon et al. (2009) and Shulgin and Hagerty (2008)
Vitrification	1	1	1	1	1	1	1	2	1	10	23	Zhao et al. (2014)
Electrokinetic	1–2	1	1	3	1	1	1	–[a]	1	10–11	28–29	Kumpiene et al. (2009), Guo et al. (2010), Terry and Banuelos (2000), Cang et al. (2009), Reddy et al. (2003), Reddy (2009) and Ouhadi et al. (2010)
Phytostabilization/phytoextraction	3	3	1	3	1	3	2	1	2	19	32	Babu et al. (2013), Alpaslan and Yukselen (2008), Chigbo and Batty (2014) and Muddarisna et al. (2013)
Enhanced bioremediation	1	1	1–2	1	1	1	2	1	3	12–13	25–26	Ren et al. (2009), Wuana et al. (2010), Srivastavaa and Thakur (2006), Sauge-Merle et al. (2012), Liu et al. (2015), Kurniati et al. (2014) and Amezcua-Allieri et al. (2005)
Sum	9–11	9	9–10	14	9	10	10	9	12–13			

1—Excellent (80–100% removal), 2—Acceptable (50–80% removal), 3—Unsatisfactory (<50% removal)

[a] Not detected

of dead biomass. Soils may become contaminated by the accumulation of heavy metals and metalloids through emissions from different resources. Different techniques are frequently listed among the best demonstrated available technologies for remediation of heavy metal-contaminated sites.

The goal of a remediation effort is to limit the extent of contamination at a hazardous waste site to prevent further deterioration of the environment and to prevent exposure by humans and other life forms to hazardous chemicals. The remedies at a given site vary depending on the properties of the chemicals found at the site, the type of soil, and the depth of contamination, and natural processes that may occur at the site. The criteria for selecting remediation technologies or treatments are: (1) short-term and long-term effectiveness at meeting the remediation goals, (2) reduction in the volume of contaminants most effectively, (3) reduction in the toxicity of contaminants, and (4) cost-effectiveness. Other factors affect the choice of remedies, for example, land disposal of hazardous materials is restricted under present environmental regulations. Because a variety of remedies can often control contamination at hazardous waste sites, selecting the appropriate technology or technologies can be a challenge.

In situ immobilization of heavy metals in contaminated soils by adding amendments has been recognized as the most cost-effective measure and easy-access method for contaminated soil remediation. Application of immobilization amendments can decrease the available fractions of heavy metals or change their redox states and thus effectively decrease the mobility, bioavailability, and toxicity of the multimetals contaminated soils with the maximum productivity duration.

Among variety of binders to immobilize heavy metals in soils, very promising results were obtained by employing rock phosphate, zeolites, calcium hydroxide, red mud, cyclonic ashes, lime, biochar, and phosphates. In particular, good results have been obtained by using hydroxyl apatite ($Ca_{10}(PO_4)_6(OH)_2$) for the immobilization of leachable Pb(II) in soils. Red mud, a by-product of the alumina industry deriving from the digestion of crushed bauxite with caustic soda, has shown some encouraging results as a heavy metal sorbent. Also, natural zeolites, a class of porous aluminosilicates characteristic of negative charges, can effectively reduce Pb, Cd, and Zn bioavailability.

The acidity and alkalinity produced from some amendments, if not controlled, pose potentially substantial environmental hazards. So more studies are needed concerning the physiology of plants treated with immobilizing agents. Noteworthy, in situ immobilization can be applied singly or combined with other remediation methods to maximize capacity of soil cleaning.

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