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Review

An overview of field-scale studies on remediation of soil contaminated with heavy metals and metalloids: Technical progress over the last decade

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ABSTRACT

Soil contamination by heavy metals and metalloids has been a major concern to human health and environmental quality. While many remediation technologies have been tested at the bench scale, there have been only limited reports at the field scale. This paper aimed to provide a comprehensive overview on the field applications of various soil remediation technologies performed over the last decade or so. Under the general categories of physical, chemical, and biological approaches, ten remediation techniques were critically reviewed. The technical feasibility and economic effectiveness were evaluated, and the pros and cons were appraised. In addition, attention was placed to the environmental impacts of the remediation practices and long-term stability of the contaminants, which should be taken into account in the establishment of remediation goals and environmental criteria. Moreover, key knowledge gaps and practical challenges are identified.

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| List o | of acronyms | PASP PC | Polyaspartic acid Portland cement | | | |
|--|---------------------------------------|-------------------|---|--|--|--|
| ACC | 1-aminocyclopropane-1-carboxylic acid | PFA | Pulverized fuel ash | | | |
| CAC | Calcium aluminate cement | PGP | Plant growth promoting | | | |
| CEC | Cation exchange capacity | pH _{PZC} | pH of point of zero charge | | | |
| CMC | Carboxymethyl cellulose | PR | Phosphate rock | | | |
| CMP | Calcium magnesium phosphate | PRBs | Permeable reactive barriers | | | |
| EDTA | Ethylenediaminetetraacetic acid | SBET | Simplified bioaccessibility extraction test | | | |
| EPA | Environmental Protection Agency | SEPs | Sequential extraction procedures | | | |
| EPSs | Extracellular polymeric substances | SOM | Soil organic matter | | | |
| GCA | Glucomonocarbonic acid | SPLP | Synthetic precipitation leaching procedure | | | |
| GGBS | Ground granulated blast furnace slag | SRB | Sulfate reducing bacteria | | | |
| GLDA | Glutamate-N,N-diacetic acid | SRC | Sulfate resistant Portland cement | | | |
| ISA | Iminodisuccinic acid | TCLP | Toxicity characteristic leaching procedure | | | |
| MAP | Mono-ammonium phosphate | UCS | Unconfined compressive strength | | | |
| Nano-HAP Nanoparticle calcium hydroxyapatite | | ZVI | Zero valent iron | | | |
| NG | NovoGro | | | | | |
| | | | | | | |
| | | | | | | |

1. Introduction

Rapid industrialization and urbanization have resulted in widespread contamination of soil with a host of heavy metals and metalloids, such as chromium (Cr), arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), selenium (Se), zinc (Zn), and nickel (Ni). There have been over 10 million major contaminated sites worldwide, of which more than 50% were contaminated with heavy metals and/or metalloids (Khalid et al., 2016). In the U.S., around 600,000 ha of land (especially at the brown-field sites) have been found contaminated with heavy metals, and the U.S. Environmental Protection Agency (EPA) has designated more than 50,000 heavy metals polluted sites as the national priority sites, which require urgent remediation actions (Ensley, 2000). In China, the average contents of Cd, Hg, As, Cu, Pb, Cr, Zn, and Ni in soil have been found to have exceeded the regulation levels by 7.0%, 1.6%, 2.7%, 2.1%, 1.5%, 1.1%, 0.9%, and 4.8%, respectively, according to the Ministry of Environmental Protection and Ministry of Land and Resources of China (Bulletin on Natural Survey of Soil Contamination in 2014).

Heavy metals and metalloids have been a major threat to human and environmental health due to their non-biodegradability, toxicity, persistence, and bioaccumulation in the food chain. They have been found responsible for causing various disorders in humans including cardiovascular diseases, cancer, cognitive impairment, chronic anemia, and damage of kidneys, nervous system, brain, skin, and bones (Järup, 2003). For instance, exposure to lead has been associated with improper hemoglobin synthesis and tumor infection, elevated blood pressure, and dysfunction of reproductive system (Pourrut et al., 2011). Consequently, it is imperative to develop and deploy innovative and site-specific remediation technologies for efficient clean-up of heavy metals or metalloids contaminated sites.

To remediate soil contaminated with heavy metals or metalloids, many studies have been carried out at the bench scale and under well controlled conditions (Ye et al., 2017a, 2017b). However, due to the complexity of the actual soil biogeochemical conditions, the technical effectiveness and feasibility can greatly deviate from laboratory results. In addition, many practical issues, such as material deliverability, soil phase mass transfer and reaction rates, impacts of delivered chemicals on the local biogeochemical conditions, and the long-term stabilities of immobilized contaminants, remain to be addressed through systematic field-scale studies and long-term monitoring under real-world environmental conditions.

Over the last decade or so, various physical, chemical, and biological processes have been aimed at reducing the total concentrations and/or bioavailable fractions of heavy metals or metalloids in order to mitigate the subsequent accumulation along the food chain (Bhargava et al., 2012) (Fig. 1). To reduce the total contaminant mass in soil, a number of remediation methods have been practiced, including soil replacement (Douay et al., 2008), electrokinetic removal (Giannis et al., 2009), thermal treatment (Busto et al., 2011), soil washing (Hu et al., 2014), and phytoextraction (Mahar et al., 2016). On the other hand, to mitigate bioavailability or bioaccumulation, various chemical immobilization techniques are often employed using a range of chemical compounds, such as lime (Wu et al., 2016), phosphate compounds (Qayyum et al., 2017; Sun et al., 2018), and organic compounds (Basta et al., 2001; Li et al., 2016; Placek et al., 2016); in addition, vitrification (Mallampati et al., 2015), solidification/stabilization (Wang et al., 2014a), and phytostabilization (Cheng et al., 2016) have also been investigated at the field. However, most of the field cleanup actions are often practiced by remediation industries. As a result, information is often less systematic or long-term monitoring of completed site is lacking. In addition, the environmental impacts of the remediation practices are often ignored. To our knowledge, most documents and reviews on the heavy metal remediation technologies have been focused on lab-scale results (Khalid et al., 2016; Yao et al., 2012). Bolan et al. (2014) reviewed some remediation technologies focusing on laboratory and greenhouse studies using a various

Remediation of soil contaminated with heavy metals



Fig. 1. Remediation technologies used for soil contaminated with heavy metals at the field scale. The remediation techniques can be broadly divided into three categories: physical, chemical, and biological processes. Physical remediation methods include (1) soil replacement, (2) vitrification, (3) electrokinetic remediation, and (4) thermal treatment; chemical approaches are comprised of (5) chemical immobilization, (6) solidification/stabilization, and (7) soil washing; and biological methods generally include (8) phytoremediation (phytovolatilization, phytoextraction, and phytostabilization), (9) microbial remediation, and (10) microbial assisted phytoremediation.

mobilizing and immobilizing soil amendments, with four field case studies on soil washing and chemical stabilization methods. Yet, comprehensive reviews on field-scale applications have been very limited over the last decade or so. Consequently, a thorough review is needed to connect the dots and to synthesize the information in order to evaluate the state of the technology and identify future research needs.

The main purpose of this review was to provide a comprehensive overview of the remediation practices performed under field conditions for remediation of soil contaminated with heavy metals and/or metalloids. Specifically, the review aimed to: (1) evaluate the technical effectiveness of various remediation technologies that have been applied at the field scale; (2) elucidate the underlying technical principles; (3) assess the technical applicability, limitations, ecological impacts, and cost effectiveness, and (4) identify critical knowledge gaps and future research needs. This review will provide useful information for both the industries and scientific research community to develop innovative remediation technologies and for site managers to adopt the most suitable remediation techniques under specific site conditions.

2. Sources and chemical speciation of heavy metals and metalloids and regulatory trend

Both natural and anthropogenic sources can lead to serious soil contamination by metals/metalloids, although the latter is often blamed to be the culprit in the modern time. Natural sources may include geological breakdown of parent rock materials and volcanic eruptions. The earth crust is composed of 95% of ingenious rocks and 5% of sedimentary rocks (Thornton, 1981). Typically, basaltic ingenious rocks contain high concentrations of Co, Cd, Zn, Cu, and Ni, whereas shales contain large amounts of Zn, Cu, Mn, Cd, and Pb (Khalid et al., 2016). In soil/groundwater systems, these heavy metals exist as carbonates, sulfides, oxides or salts. Anthropogenic sources are primarily associated with refining and mining of ores, batteries, paper industries, tanneries, fertilizer and pesticides industries, biosolids application, wastewater irrigation, and atmospheric depositions and combustion of fossil fuels (Mahar et al., 2016). Heavy metals can be released in inorganic, organic, and/or elemental forms. Ross (1994) divided the anthropogenic sources of heavy metals into five groups, namely, (1) agricultural (Zn, As, Pb, Cd, Cu, Se and U), (2) metalliferous mining and smelting (Cd, Pb, As and Hg), (3) industrial (Cd, Hg, As, Cr, Cu, Co, Ni and Zn), (4) waste disposal (As, Pb, Cu, Cd, Cr, Zn and Hg), and (5) atmospheric deposition (As, Pb, Cr, Hg, Cu, Cd and U).

Heavy metals can be bound to various compartments in soil, namely, amorphous materials, clay surfaces or iron/manganese oxyhydroxides, lattice of secondary minerals like carbonates, sulfates or oxides, organic matter or lattice of primary minerals such as silicates (Tessier et al., 1979; Yu et al., 2001). Because soil adsorption or solid-phase speciation can greatly impact the mobility and availabilities of metals/metalloids, it has been increasingly recognized that the toxicity and reactivity are often governed by the available fraction of the contaminants, rather than the total contaminant concentration. Namely, specific chemical speciation of metals/metalloids (Nyamangara, 1998) as well as interactions with various soil components including soil organic matter (SOM) should be taken into account in establishing remediation goals.

To determine the relative availabilities of metals/metalloids in soil, various sequential extraction procedures (SEPs) are often employed (Guevara-Riba et al., 2004). These operationally defined methodologies use a series of selective extracting reagents to successively dissolve different fractions of metals/metalloids that are bound with various fractions of mineralogical components (Gleyzes et al., 2002). For instance, the SEP by Tessier et al. (1979) operationally divides soil-bound heavy metals into five geochemical forms, i.e., water-soluble and exchangeable, carbonate bound, iron and manganese oxide associated, organic matter bound and residual forms. The water-soluble and exchangeable fractions are considered to be the most available components; and the fractions bound to carbonate, oxide, and organic matter are supposed to represent the potentially bioavailable components under changing conditions; whereas the residual fraction represents the most stable form associated with anthropogenic or geogenic components, which is considered unavailable to plants or microorganisms.

From a soil remediation standpoint, the general trend has been shifting from reduction of the total concentration to reduction of the physic-chemically and/or biologically available fractions of metals. This regulatory shift represents a tremendous saving in remediation cost. While metals are not degradable, their speciation and binding with soil may be manipulated through various amending reagents or materials, thereby reducing their solubility,

Table 1

Comparison of remediation technologies used for metals/metalloids contaminated soil at the field scale.

| Remediation te | echnology | Description | Advantages | Disadvantages |
|---------------------------|-------------------------------------|--|---|--|
| Physical remediation | Soil replacement | Use of non-contaminated soil to replace or partly replace contaminated soil | Feasible for small volumes of heavily polluted shallow soil in small area | Costly, the removed contaminated soil may need further handling and disposal, may not be applicable to agricultural sites due to the associated high cost and potential loss of soil fertility |
| | Vitrification | Use of high temperature to melt the soil and to stabilize heavy metals after cooling within a solidified vitreous mass | Permanent remedy with good long-term effectiveness, potential volume reduction of materials, products with potential reuse options, wide application range | Costly, big power loss, off gases may be created and must be treated, not suitable for large area repair |
| | Electrokinetic remediation | Application of electrical current on two sides of the electrolytic tank containing saturated contaminated soil | Applicable for saturated soils with low groundwater flow, short repair time, low energy consumption, complete repair | Limited treatment depth, any heterogeneity of the soil body decreases the effectiveness of the method |
| | Thermal treatment | Heating of the contaminated soil via steam, microwave, and infrared radiation to volatize the pollutant without combustion of the media or contaminants | Simple process, devices with mobility, effective extraction and recovery of mercury, and safety | High capital costs, effectiveness only at rather high total soil mercury contents, requires gas emission control and specialized facilities, easy damage of soil structure |
| Chemical remediation | Chemical stabilization | Addition of immobilizing agents to the contaminated soil to decrease the mobility, bioavailability, and bioaccessibility of heavy metals in soil | Relatively cost effective, simple, and rapid remediation approach | Cannot remove heavy metals from soil, change the physicochemical properties of soil |
| | Solidification/ stabilization | Stabilization refers to a process of adding reagents to the contaminated soil to convert a toxic waste to a physically and chemically more stable form. Solidification is a process that encapsulates the waste materials in a monolithic solid of high structural integrity. | Relatively low cost, easy use, comprehensive strength, and high resistance to biodegradation, good engineering applicability | Increased volume of the treated material, long-term monitoring is needed |
| | Soil washing | Leaching of heavy metals from soil matrix with various reagents and extractants | Permanently removes metal contaminants from soil, a rapid method, highly effective method for cleaning up strongly contaminated soil | Soil structure deterioration and high cost, nutrients can be released simultaneously from soil during the remediation process, high costs and arduous working processes |
| Biological remediation | Phytostabilization | Use of plants with ability to decrease the mobility or/and bioavailability of a metal via certain mechanisms including adsorption by roots, precipitation, and complexation in the root zone | Cost effective, non-invasive, no secondary pollution | Limited repair capacity and treatment depth, long repairing cycle, plants and soil require long-term monitoring |
| | Phytoextraction | Uptake of contaminants from soil by plant roots and their translocation and accumulation in aboveround biomass | | |
| | Phytovolatalization | Uptake and transpiration of metal into volatile form and its release into the atmosphere through stomata | | |
| | Microbial remediation | Process of using microorganisms (i.e., bacteria, fungi, and algae) to induce adsorption, precipitation, oxidation, and reduction of heavy metals in soil | | |
| | Microbial assisted phytoremediation | Assistance of plant growth promoting bacteria together with phytoremediation | | |

mobility, and bioavailability. Accordingly, remediation goals are often based on leachabilities of soil-sorbed metals/metalloids. For instance, the toxicity characteristic leaching procedure (TCLP) (EPA Method 1311) has been widely used in the U.S. and many other countries to gauge remediation effectiveness or identify hazardous materials, where the thresholds are often set at 100 times the corresponding maximum contaminant level (MCL) in drinking water. In China, sulfuric acid and nitric acid method (HJ/T299-2007) has been used in measuring the degree of success in remediation of metals/metalloids contaminated soil.

3. Field-scale remediation technologies

Depending on the type of heavy metals/metalloids and site characteristics, different remediation technologies may be applied. Table 1 summarizes the most commonly used physical, chemical, and biological processes. Given the complex nature of soil biogeochemical conditions and the distribution of contaminants, various remediation approaches are often combined to achieve the remediation goals.

3.1. Physical remediation

3.1.1. Soil replacement

Soil replacement relies on the use of non-contaminated soil to replace or partly replace the contaminated soil, aiming to dilute the heavy metal contents in soil, to increase the soil environmental capacity, and thus remediate the soil (Derakhshan Nejad et al., 2017). Prior to 1984, excavation, off-site disposal, and soil replacement were the most commonly methods for cleaning up contaminated sites.

Douay et al. (2008) carried out soil replacement remediation at three kitchen gardens (Garden 1, 2, and 3) situated less than 1 km from the Metaleurop Nord smelter in northern France. The sites were contaminated with high concentrations of Pb and Cd (up to 3300 and 24 mg/kg, respectively) in the top soil. They delineated a surface area of 80 m² for Garden 1, 50 m² for Garden 2, and 100 m² for Garden 3, and replaced 28 m³, 17.5 m³ and 40 m³ of the contaminated soil with a local clean soil, respectively. After the soil replacement, cultivation of vegetables showed a clear improvement of vegetables Cd and Pb levels in radish leaves were reduced

from 26.2 mg/kg and 41.2 mg/kg to 3.0 mg/kg and 8.4 mg/kg, respectively, after the remediation action. The replaced contaminated soil was exported to Metaleurop Nord for the use of slag heap coverage.

This technique is costly due to intensive labor and is feasible for small volumes of heavily polluted shallow soil in small area. In addition, the removed contaminated soil often falls into the category of hazardous wastes, demanding costly further handling and disposal. It may not be applicable to agricultural sites, which are characterized of large volume of soil and low concentration of contaminants, due to the associated high cost and potential loss of soil fertility, and may be limited by the availability of the clean replacement soil.

3.1.2. Vitrification

Vitrification is a high temperature process in which organic matter is incinerated and mineral matter is melted, leading to the sequestration of metals/metalloids in a small volume of vitreous material (Mallampati et al., 2015). Vitrification can be applied both *in situ* and above ground in a treatment unit (*ex situ*). Two primary heat sources include thermal energy by using combustion of fossil fuels and electrical energy through the Joule effect, electric arc, induction, or plasma processes (Colombo et al., 2003). During vitrification, some metal species such as Hg may be volatilized, which may be subject to regulatory constraints and require additional handling and treatment.

Dellisanti et al. (2009) carried out an in-field Joule heating vitrification of tons of Zn– and Pb-rich ceramic waste (Fig. 2). They reported that heating the waste up to about 1850 °C completely melted the waste material and the rapid cooling formed a monolithic glassified material of 55 tons, which effectively immobilized the heavy metals and non-volatile inorganic compounds. Wang et al. (2008a) conducted a pilot-scale experiment to treat a fly ash from a municipal solid waste incinerator using a diesel oil furnace for more than six months. They observed that the residual levels of stabilized heavy metals (Cd, Cr, Cu, Pb, and Zn) in the melted slag followed the order of Cr > Zn > Cu > Cd > Pb, and that the TCLP-leachable concentrations of all the heavy metals were far below the regulatory values.

Temperature is the key factor in terms of both immobilization effectives and process cost. While traditional fuel-based or electrical heating is often cost prohibitive, recent solar technology may facilitate remarkable energy saving. For example, Navarro et al. (2013) investigated the vitrification of hazardous mine wastes and mine tailing from old mercury and Ag–Pb mines in Spain using solar technology, and observed successful immobilization of Fe, Mn, Ni, Cu and Zn at 1350 °C.

In addition, the electrical conductivity of the target soil/waste may limit the effectiveness. As soil vitrification involves insertion of electrodes into the soil, it is critical for the medium to be able to carry electrical current. Thus, a main limitation of *in situ* vitrification is the potential of the soil to melt so that current can pass through it. Soil containing high alkali (e.g., 1.4 wt %) may not be a good conductor (Buelt and Thompson, 1992). Therefore, *in situ* vitrification can be performed only for wet soil with low alkali content. This technique can be applied for small-scale remediation of heavily polluted sites. It permanently remediates the soil with long-term effectiveness and much reduced waste volume, and may produce products with potential reuse options. However, under field conditions or at large scale, this technique can be highly expensive.

3.1.3. Electrokinetic remediation

Electrokinetic remediation is a new and effective physical method for remediation of soil contaminated with heavy metals or metalloids. As depicted in Fig. 3, this technique relies on an electric field gradient of suitable intensity that is established across an electrolytic tank containing saturated soil. The electrodes are generally immersed into constructed wells containing an electrolytic solution. Under the electric field, the target metal ions migrate towards the oppositely charged electrodes. The contaminants accumulated at the electrodes are then treated with various physical-chemical approaches, including electroplating. precipitation/co-precipitation, pump-and-treat the water near the electrodes, or sorption with ion-exchange resins (Reddy et al., 2001).

Rosestolato et al. (2015) carried out a field-scale project on electrokinetic remediation of 400 kg of a mercury contaminated soil, and found that about 60% of total Hg was removed in less than 3 months. Kim et al. (2012) applied an *in situ* electrokinetic technique to clean up multiple metals/metalloids in a contaminated rice field, and they observed that 39.8%, 17.2%, and 19.4% of As, Cu and Pb, respectively, were removed after 4 weeks of the treatment. Earlier, Kim et al. (2011) carried out a pilot-scale electrokinetic test and achieved 96.8% removal of uranium from a uranium contaminated soil after 25 days.







Fig. 3. (a) Electrokinetic treatment of ionic contaminants in soil; and (b) A conceptualized representation of the main mechanisms in electrokinetic remediation (Cameselle et al., 2013a).

The main mechanisms of electrokinetic remediation include electrophoresis (movement of charged particles), electric seepage or electro-migration (movement of charged chemicals), electroosmosis (fluid movement), and electrolysis (redox reactions induced by the electric current) (Yao et al., 2012). Electro-migration is one to two orders of magnitude faster than the other mechanisms, and thus is the dominant mass transfer mechanism for heavy metals/metalloids (Virkutyte et al., 2002). Electrolysis of water is the dominant electron transfer reaction occurring at electrodes during the electrokinetic process:

$$H_2 O \rightarrow 2H^+ + \frac{1}{2}O_2(g) + 2e^- (Anode)$$
 (1)

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2(g) \text{ (Cathode)}$$
 (2)

The H⁺ ions produced at the anode decrease the local pH, which is conducive to desorption of metallic cations from the soil phase because of the elevated competition of H⁺ ions and more positive soil surface potential, and adsorption of oxyanions such as arsenate. Conversely, OH⁻ ions at the cathode cause an increase of pH, which is in favor of soil adsorption of heavy metals or formation of precipitates as hydroxides and oxyhydroxides. In addition, the H⁺ ions at the anode may migrate through the soil towards the cathode, whereas the OH⁻ ions migrate towards the anode. Depending on the extent of migration of H⁺ and OH⁻, pH may vary across the soil. The high pH region in the proximity to the cathode is the main obstacle to heavy metal removal from the soil.

To improve the effectiveness, surfactants (e.g., Tween 80, Tween 20, and rhamnolipid biosurfactant) and complexing agents (e.g., humic substances, citric acid, ammonium acetate, nitrilotriacetic

acid, diethylenetriamine pentaacetic acid, and ethyleneglycol tetraacetic acid) have been applied (Alcántara et al., 2012; Ammami et al., 2015; Bahemmat et al., 2016; Chen et al., 2011; Falciglia et al., 2016; Fu et al., 2017; Giannis et al., 2009; Maturi et al., 2009). Ethylenediaminetetraacetic acid (EDTA) is a strong metalcomplexing agent that can extract and enhance the mobility of heavy metals from soil (Hanay et al., 2009) and has been applied successfully in the field. Jeon et al. (2015) remediated a paddy rice soil contaminated with Pb and Cu via an *in situ* electrokinetic process using EDTA as an electrolyte to enhance the metals extraction. The negatively charged metal-EDTA complexes were transported towards the anode. As a result, 40.3% of Cu and 46.6% of Pb were removed from the soil after 24 weeks of operation.

Electrokinetic remediation is also used in combination with other processes such as microbial process (Lee and Kim, 2010), phytoremediation (Cameselle et al., 2013b), and permeable reactive barriers (PRBs) (Zhao et al., 2016). Chung (2009) combined electrokinetic treatment with PRB to remediate a Cu-contaminated site. The perforated cathode pile was filled with reactive materials. Consequently, the migrating Cu^{2+} ions in the soil were adsorbed at the cathode. After 30 days of operation, the Cu removal reached 68.7%, 93.7%, 75.0%, 88.0%, and 4.7%, respectively, when iron powder, zeolite, slag powder, tire chip, and sand were used.

The advantages of electrokinetic remediation include: (1) it produces no or little by-products, (2) it is easy to install and operate and effective for soil with low permeability, (3) it does not abolish the original nature of the soil, and (4) the treatment duration is relatively short. However, this technique bears with some critical drawbacks, including: (1) it is only applicable for saturated soil with low groundwater flow, (2) it only removes a part of leachable metals/metalloids, (3) it is less effective for heterogeneous soil, (4) the energy cost can be prohibitive especially when higher removal is required, and (5) the application of the electrical field may cause fluctuation in soil pH or significant alteration in local biogeochemical conditions.

3.1.4. Thermal treatment

Thermal treatment is a physical process based on the volatility of contaminants. While the process is more suitable for volatile organic compounds, it has been used for removal of volatile metals such as Hg. It is performed by heating contaminated soil via steam, microwave, or infrared radiation without combustion or melting of the media or contaminants. The volatilized metals are then collected under negative pressure or with a carrier gas. Compared to vitrification or incineration, thermal treatment is much less energy-intensive and has the advantage that it can simultaneously remove volatile compounds that are often co-present with metals/ metalloids.

Inorganic mercury is usually present in soil in the elemental state or as mercurial compounds such as HgS, HgO, and HgCO₃. Thermal treatment can covert the mercurial compounds into the gaseous elemental mercury. The main components of a thermal desorption system include a pre-treatment and material handling unit, a desorption unit, and a post-treatment unit for treatment of off-gas and processed soil. The pre-treatment involves physical screening to remove extraneous matter such as plastic or rubber and dewatering to achieve suitable moisture content. A thermal desorption unit was employed to remove Hg from the pre-treated media, which was operated at temperatures from 320 to 700 °C (USEPA, 2007). The high temperature converts mercury into its gaseous form, which is then collected and further treated. It is one of the few methods that have been applied to the field for removing very high concentrations of Hg (>260 mg/kg) in soil.

Temperature and treatment time are the main factors determining the decontamination levels as well as the process cost (Wang et al., 2012a, 2012b). Greater efficiency is achieved at relatively higher temperatures, e.g. from 460 to 700 °C (Busto et al., 2011; Richter and Flachberger, 2010). Hseu et al. (2014) reported that heating soil to 550 °C for 1 h was able to remove 99% of Hg. Moreover, thermal treatment at high temperatures may alter the soil properties and cause the coexisting contaminants, especially trace metals, to transform and repartition. Huang et al. (2011) found that thermal treatment at >550 °C reduced the mercury content from 1320 to 6 mg/kg, and altered the binding forms of Cr, Cu, and Ni from those associated with Fe/Mn oxides into acid-extractable, organic-matter bound, and residual forms, which are less mobile.

High energy consumption has been a major concern of this technology. To reduce energy consumption, thermal treatment may be operated at a lower temperature for a longer time. Kucharski et al. (2005) operated thermal treatment at 100 °C for 10 days for remediation of a mercury-contaminated soil, and was able to achieve 32% mercury removal without negative effects on the growth properties of the soil.

The advantages of this method include easy and safe implementation, mobility of treatment devices, effective extraction and recovery of mercury, and in particular, simultaneous removal or immobilization of co-contaminants. The major shortcoming is the high energy consumption and capital costs due to the high temperature requirement and the specialized facilities required. Consequently, this technology has been solely used for soil containing very high mercury as far as heavy metals are concerned. Thermal treatment alters soil properties which can affect certain functions of soil. It can cause degradation of SOM and changes of soil texture and mineralogy. Combustion of SOM leads to the loss of C and N, altering the available nutrients and elements for plants. Moreover, soil heating is detrimental to microorganisms such as pathogens, bacteria, and fungi (O'Brien et al., 2018).

3.2. Chemical remediation

3.2.1. Chemical stabilization

Chemical stabilization is a remediation process in which immobilizing agents are added to contaminated soil to decrease the mobility, bioavailability, and bioaccessibility of heavy metals in soil. Heavy metals can be immobilized by surface complexation, chemical precipitation, ion exchange, and adsorption, thus limiting the transport and bioavailability of heavy metals in soil (Porter et al., 2004). The most commonly applied amending agents in the field include clay minerals, phosphate compounds, liming materials, organic composts, metal oxides, and biochar (Table 2). Chemical stabilization is a relatively cost effective, simple, and rapid remediation approach. However, it does not remove the heavy metals from soil. Consequently, the long-term stability should be monitored.

3.2.1.1. Clay minerals. Clay minerals are generally regarded as the fine particles contained in the colloidal fraction of soil and sediment. They can act as a natural scavenger of heavy metals through ion exchange, adsorption, and surface processes such as precipitation, nucleation and crystallization (Yuan et al., 2013). Clay minerals, such as aluminosilicates, sepiolite, palygorskite, and bentonite, have been widely used for immobilization of heavy metals at the field scale (Liang et al., 2014; Sun et al., 2015, 2016). These naturally abundant materials have the advantages of being green, low-cost, and effective for performance host of heavy metals or metalloids.

Sepiolite $(Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O)$ is a porous fibrous hydrated magnesium silicate. It is composed of blocks of two tetrahedral silica sheets, which sandwich an octahedral sheet of magnesium oxide/hydroxide. There are discontinuities and inversions in the

 Table 2

 Chemical amendments for immobilization of heavy metals or metalloids in soil and groundwater at the field scale.

| Amendments | | Immobilization mechanisms | Metal immobilized | Observations | Reference |
|------------------------|--|--|--|---|---|
| Clay minerals | Sepiolite | Chemical precipitation and surface complexation | Cd | The amendments increased the paddy soil pH, significantly reduced the HCl, TCLP, CaCl ₂ , and NH ₄ OAc-extractable Cd concentrations, resulting in a notable decrease in the Cd contents in brown rice. | (Liang et al., 2014) |
| | Sepiolite | | Cd | Sepiolite obviously increased soil pH and carbonate bounded fraction of Cd in soil, remarkably reduced HCl- and MgCl ₂ -extractable | (Liang et al., 2016) |
| | Sepiolite + limestone | | Cd, Pb | of two cultivars in two consecutive years. The treatment decreased exchangeable Pb and Cd concentrations by 99.8% and 98.9%, and reduced their contents in brown rice by 81.2% and 81.0% | (Wu et al., 2016) |
| | Sepiolite | | Cd | respectively. The addition of sepiolite resulted in 4.0–32.5% reductions in TCLP extractable Cd and 22.8 –61.4% reductions in plant uptake, and improved soil microbial population and enzymatic | (Sun et al., 2016) |
| | Sepiolite + limestone | | Pb, Cd, Cu, Zn | activities. The treatment significantly increased soil pH values and cation exchange capacity, reduced exchangeable fractions and TCLP-leachability of Pb, Cd, Cu, and Zn, and inhibited their accumulation in rice plants. | (Zhou et al., 2014) |
| | Sepiolite | | Cd | Sepiolite significantly reduced NaNO ₃ , CaCl ₂ , and DTPA-extractable Cd, decreased exchangeable Cd, and increased the portions of forms of carbonate-bound, Fe/Mn oxide-bound, and residual Cd in the soils, resulting in a reduction in | l (Zhu et al., 2010) |
| | Sepiolite | | Cd | rice Cd uptake. Natural sepiolite significantly immobilized bioavailable Cd contents in paddy soil, and consequently lowered the Cd contents of brown rice, husk, straw, and roots of rice by 54.7–73.7% 44.0–62.5%, 26.5–67.2%, and 36.7–46.7%, | (Yin et al., 2017) |
| | Palygorskite | Chemical precipitation and surface complexation | Cd | respectively. Palygorskite increased the paddy soil pH, significantly reduced the HCl, TCLP, CaCl ₂ , and NH ₄ OAc-extractable Cd concentrations, reduced exchangeable Cd contents, and increased carbonate-bound and residual fractions, resulting in a notable decrease in the Cd content in brown rice | (Liang et al., 2014) |
| | | | Cd | Palygorskite reduced Cd contents in brown rice by 23.0–56.4%. | (Han et al., 2014) |
| | | | Cu, Pb, Zn, Cd, Ag, As, Mn, Ba, Sb | reduced water leachable fractions of Cu, Pb, Zn, Cd, Ag, As, Mn, Ba, and Sb by 17%, 50%, 45%, 41% 46%, 18%, 47%, 45%, and 29%, respectively, after 1 month. | (2011a015 et al., 2012) |
| | Bentonite | | Cd, Pb | The exchangeable fractions of Cd and Pb were reduced by $11.1-42.5\%$ and $20.3-49.3\%$, whereas the residual portions increased by $3.0-54.3\%$ and $6.7-10.0\%$, respectively. Treatments with bentonite inhibited Cd and Pb translocation from soil to the aerial parts of <i>Oryza sativa</i> L. The concentrations of Cd and Pb in the roots were reduced by $9.4-31.3\%$ and $5.1-26.7\%$, and by $17.4-44.3\%$ and $3.7-7.8\%$ in the shoots, respectively. | (Sun et al., 2015) |
| Phosphate compounds | Phosphate rock (Ca ₁₀ (PO ₄) ₆ Cl ₂) Calcium magnesium phosphate (Ca ₃ (PO ₄) ₂) Single superphosphate (Ca(H ₂ PO ₄) ₂) | Pb: Pb phosphate precipitation, especially pyromorphite-like mineral; Zn: Surface complexation and adsorption; Cd: Surface adsorption | Pb, Zn, Cd | The addition of P fertilizers at different dosages (50, 300, and 500 g/m ²) effectively decreased water soluble and exchangeable fractions of heavy metals by 22.0–81.4% for Pb, 1.5–30.7% for Cd, and 11.7–75.3% for Zn (exception of single superphosphate treatments with no significant difference) and TCLP Pb by 27–71%, resulting in reduced uptakes of Pb (16.0–58.0%), Cd (16.5–66.9%), and Zn (1.2–73.2%) by a Chinese green vergetable | (Wang et al., 2008b) |
| | Ammonium phosphate | Chemical precipitation and surface adsorption | Cd | The amendment increased the Cd immobilization and decreased bioavailable Cd in soil, resulting in (continued | (Qayyum et al., 2017) on next page) |

Table 2 (continued)

| Amendments | | Immobilization mechanisms | Metal immobilized | Observations | Reference |
|---------------------|---|--|----------------------|---|---|
| | Calcium hydroxyapatite (nano-HAP) | Adsorption and chemical precipitaiton | Cu and Zn | an increase in wheat growth and yield and decreased Cd accumulation in straw and grains. The addition of nano-HAP significantly decreased the TCLP-leachable and bioaccessible concentrations of Cu and Zn, and their uptake by rvegrass. The biomass of rvegrass increased as | (Sun et al., 2018) |
| Liming materials | Ca(OH) ₂ | Chemical precipitation | Cu and Cd | the nano-HAP dosage increased. The TCLP-extractable Cu concentration decreased by 7.90 mg/L compared with control and SBET extractable Cu decreased from 6.09 mg/L | (Cui et al., 2016a) |
| | Ca(OH) ₂ | Chemical precipitation | Cd and Zn | (control) to 4.65 mg/L. The application of Ca(OH) ₂ significantly decreased NH_4OAc extractable Cd and Zn | (Hong et al., 2009) |
| | Oyster shells and eggshells | Chemical precipitation | Cd and Pb | concentrations of soil and their uptake by radish. After 420 d of incubation, the exchangeable fraction of Cd evolved from 23.64% to 1.90 -3.81%, while the carbonate fraction increased fract 10.5% to 2.6 Cf. 46.26%. Similar transformed | (Lim et al., 2013) |
| Organic composts | Biosolid | Surface complexation and chemical precipitation | Cd and Zn | from 19.59% to 36.66–46.36%. Similar trend was also observed for Pb. As a result, the TCLP- leachable Cd and Pb were effectively reduced. Lime-stabilized biosolid greatly reduced the phytoavailability of Cd and Zn in Cd–, Pb–, and Zn-contaminated soils from smelter sites in Olubhema | (Basta et al., 2001) |
| | Biosolid | | Cd, Zn, and Pb | The treatment increased soil pH, cation exchange capacity, and humic acids, leading to an improvement of sorption capacity of the soil. The readily soluble forms of trace elements and the | (Placek et al., 2016) |
| | Chicken manure compost | | Cd | leaching of biogenic components were reduced. The compost increased soil pH, total phosphorus content, and organic matter, and enhanced soil biological properties. Moreover, the treatment decreased the acid-extractable Cd by $8.2-37.6\%$, while increased the reducible and oxidisable Cd by $9.2-39.5$ and $8.2-60.4\%$ respectively. | (Li et al., 2016) |
| Metal oxides | Iron oxides | Adsorption and/or co-precipitation | As | The amendments effectively immobilized As in a paddy soil and prevented As transfer from soil to pore water and crops. | (Ko et al., 2015) |
| | Fe oxides/hydroxides | | As | Injection of dissolved Fe(II) and NaClO into the As-contaminated aquifer promoted the formation of Fe oxides/hydroxides, which effectively oxidized As(III) into As(V), and thus removed aqueous As | (Xie et al., 2016) |
| | Ferric oxyhydroxide powder + limestone | Specific sorption, co-precipitation, and inner- sphere complex | Pb, Sb | The treatment resulted in an average decrease of Sb and Pb in pore water by 66% and 97%, respectively, and remained stable over four year. Sb and Pb was transformed to amorphous iron oxides or even more crystalline and residual mineral phases | (Okkenhaug et al., 2016) |
| | Mn oxides | | Pb | A dosage of 10% effectively immobilized Pb for a | (McCann |
| Biochar | What straw biochar | Increase in soil pH, total organic carbon, abundant functional groups and complex structures of biochar, leading to a reduction in the extractable fractions of heavy metals. | Cd | Biochar treatment greatly reduced Cd content in rice grain by 20–90%, resulting in a safe Cd level (<0.4 mg/kg) of rice grain from all Cd- contaminated rice fields at a biochar dosage of 40 t/ha expect the site with a Cd content over | et al., 2015) (Bian et al., 2013) |
| | | | Cd and Pb | The soil extractable Cd and Pb were decreased. As a result, the Cd contents in rice plant tissues and Pb in root tissues were similarity reduced | (Bian et al., 2014) |
| | | | Cd | The treatment significantly decreased CaCl ₂ - extractable Cd, and Cd contents in rice tissue and in rice grain | (Bian et al., 2016) |
| | | | Cd and Zn | Biochar significantly reduced Cd and Zn availability by up to 85% and 91% in an acidic paddy soil when incorporated at rates of 20 and 40 t/ha. | (Chen et al., 2016a) |
| | | | Cd and Pb | Biochar significantly transformed the exchangeable fractions of Cd and Pb into relatively stable fractions (residual and organic). | (Cui et al., 2016b) |
| | Sugarcane bagasse biochar | | Cd, Cu, and Pb | The exchangeable Cd was reduced whereas organically-bound fraction increased with increasing biochar rate. The bioavailability of | (Nie et al., 2018) |

 Table 2 (continued)

| Amendments | Immobilization mechanisms | Metal immobilized | Observations | Reference |
|------------|---------------------------------|----------------------|--|----------------|
| | | _ | heavy metals to plant shoots and roots decreased with increasing biochar dosage. | |
| | Wood biochar | As, Cu, Zn, | Biochar caused changes in metal fractionation in | (Lucchini |
| | | Cd, and Ni | soil, and showed no negative effects on crop or soil quality. | et al., 2014) |
| | Holm oak chips biochar | As, Cd, Cu, | Biochar stabilized Pb and Cd, while marginally | (Moreno- |
| | | Ni, Pb and | increased As mobilization, resulting in a | Jiménez |
| | | Zn | reduction of Cd and Pb in barley grain whereas As | et al., 2016) |
| | | | content slightly increased. | |
| | Rice straw biochar | Cu, Pb, and | Biochar treatment decreased bioavailability of | (Niu et al., |
| | | Zn | heavy metals, reduced contents of heavy metals | 2015) |
| | | | in vegetables, and increased vegetable yields. | |
| | Sewage sludge biochar | Cd | The treatment significantly decreased Cd | (Zhang et al., |
| | | | contents in rice grains, and increased grain yields. | 2016) |
| | Miscanthus | Cd, Zn, and | CaCl ₂ -extractability of metals significantly | (Houben |
| | (Miscanthus \times giganteus) | Pb | decreased with increasing rates of biochar after | et al., 2013) |
| | straw biochar | | 1 h of incubation. | |
| | British broadleaf | Ni and Zn | Biochar enhanced the residual fraction of Ni and | (Shen et al., |
| | hardwood biochar | | Zn in the soils. Ni and Zn concentrations in the | 2016) |
| | | | carbonic acid leaching tested were reduced by 83 -98% over three years. | |

silica sheet in sepiolite, which give rise to its structural tunnels and blocks (Akçay, 2004). These tunnels contain H₂O molecules and exchangeable cations (K⁺ and Ca²⁺). In the inner blocks, all corners of the silica tetrahedral are connected to adjacent blocks; whereas in the outer blocks, some of the corners are Si atoms bound to hydroxyls (Si–OH). These Si–OH groups are the main active centers for metal polycations (Tekin et al., 2006). Palygorskite, (Mg,Al)₂Si₄O₁₀(OH)·4H₂O, is a magnesium aluminum phyllosilicate with a fibrous morphology, large specific surface area, moderate cation exchange capacity (CEC), and good adsorptive properties.

The remediation effectiveness of sepiolite and palygorskite has been confirmed in many field demonstrations as shown in Table 2. For instance, Liang et al. (2014) conducted a field demonstration experiment in Chenzhou, Hunan province, China, utilizing sepiolite and palygorskite as amendments to in situ immobilize Cd in soil and thereby reducing accumulation of Cd in brown grains of rice. After 30 days of the amendments, the paddy soil pH was increased, whereas the HCl-, TCLP-, CaCl2-, and NH4OAc-extractable Cd concentrations were significantly reduced, resulting in a notable decrease in the Cd content in the brown rice. Chemical precipitation and surface complexation were the main immobilization mechanisms. Sun et al. (2016) investigated the effectiveness and stability of sepiolite for immobilization of Cd-polluted soil through a three-year field experiment. The addition of sepiolite resulted in a 4.0-32.5% reduction in TCLP extractable Cd and a 22.8-61.4% reduction in plant uptake, and improved the soil microbial population and enzymatic activities.

Bentonite, a 2:1 type of aluminosilicate, is a kind of expandable clay composed primarily of montmorillonite. Due to the isomorphic substitution within the aluminosilicate sheets, bentonite is characterized by high permanent negative charges and large specific surface area. The negative net charge is balanced by exchangeable cations adsorbed between the unit layers and around their edges (Narayanan and Deshpande, 1998). Bentonite has been applied effectively for remediation of paddy soil polluted with Cd and Pb in pot trials (Sun et al., 2015). After 5 weeks of bentonite application at dosages of 0.5–5%, the exchangeable fractions of Cd and Pb were reduced by 11.1–42.5% and 20.3–49.3%, respectively, whereas the residual portions increased by 3.0–54.3% and 6.7–10.0%. The treatments inhibited Cd and Pb translocation from soil to the aerial parts of *Oryza sativa* L. The concentrations of Cd and Pb in the roots were reduced by 9.4–31.3% and 5.1–26.7%, and by 17.4–44.3% and

3.7-7.8% in the shoots, respectively.

There are several limitations associated with the use of clay minerals. First, it is difficult to deliver the minerals into the deep contaminated zones, and thus limiting their uses for *in situ* soil remediation; Second, the reaction rate is limited by the desorption rate of heavy metals or metalloids from soil; Third, mechanical mixing is usually needed for field soil treatment; Fourth, clay minerals have limited sorption capacity and selectivity for metals, as such, large dosages are usually required and the immobilized metals/metalloids are likely to be remobilized. There is a need to enhance the remediation effect and reduce the dosage to lower costs. In addition, long-term monitoring is needed to evaluate the long-term stability.

3.2.1.2. Phosphate compounds. Soluble phosphate compounds and particulate phosphate minerals have been widely studied for immobilization of heavy metals. Commonly used phosphate minerals include both natural and synthetic apatite and hydroxyapatite, whereas soluble phosphate compounds include phosphate salts and phosphoric acid. In principle, phosphate containing minerals immobilize heavy metals through direct metal adsorption/substitution, phosphate induced metal adsorption or surface complexation, and chemical precipitation of metals (Bolan et al., 2003a, 2003b). Soluble phosphates can react with multivalent metal cations to form insoluble metal orthophosphates akin to naturally occurring minerals which are usually sparingly soluble (with a low solubility product, K_{sp}) and are stable in the natural biogeochemical environment. Phosphate can form strong complexes or precipitates with many common heavy metals, such as Pb $(K_{sp} \text{ of } Pb_5(PO_4)_3Cl = 10^{-84.4})$ (Ruby et al., 1994), Cd (e.g., Cd₃(PO₄)₂OH, $K_{sp} = 10^{-42.5}$), and Cu (K_{sp} of Cu₅(PO₄)₃Cl = $10^{-54.0}$; Cu₅(PO₄)₃OH, $K_{sp} = 10^{-51.6}$) (Eighmy et al., 1997; Eighmy and Dykstra Eusden, 2004).

Field-scale applications of phosphate compounds to immobilize heavy metals have gained growing momentum over the last decade. Wang et al. (2008b) undertook a field demonstration using commercial phosphate fertilizers including phosphate rock (PR) and calcium magnesium phosphate (CMP) at a site heavily contaminated by Pb, Zn, and Cd from lead and zinc mining tailings in Shaoxing, Zhejiang, China. They found that the addition of the PR and CMP fertilizers at different dosages (50, 300, and 500 g/m²) effectively decreased water soluble and exchangeable fractions by



Fig. 4. Bioavailability or leachability of Cu and Zn in soil treated with hydroxyapatite nanoparticles (nano-HAP), when extracted by (a) CaCl₂ and (b) TCLP procedure (Sun et al., 2018).

22.0–81.4% for Pb, 1.5–30.7% for Cd, and 11.7–75.3% for Zn and TCLP extractable Pb by 27–71%, resulting in reduced uptakes of Pb (16.0–58.0%), Cd (16.5–66.9%), and Zn (1.2–73.2%) by a Chinese green vegetable *Brassica chinensis* L. *campestris.* Qayyum et al. (2017) reported that the application of mono-ammonium phosphate (MAP) in a Cd-contaminated field significantly enhanced Cd immobilization and decreased bioavailable Cd in soil, resulting in an increase in wheat growth and yield and an decrease in Cd accumulation in the straw and grains.

Nanoscale materials have shown great potential for soil remediation due to their small particle size, large specific surface area, high reactivity, and improved soil deliverability. Sun et al. (2018) found that nanoscale calcium hydroxyapatite (nano-HAP) was effective for immobilizing Cu and Zn in a heavy metal polluted soil near a smelting factory. The addition of nano-HAP at 1%, 3%, and 5% reduced the acid-soluble fraction of Cu by 9.3%, 24.4%, and 35.7%, respectively, while the reducible and oxidizable fractions of Cu were increased by 5.5% and 83.5%, respectively, at 5% of the nanoparticles. As a result, the CaCl₂ extractable concentrations of Cu and Zn were reduced by 67.8%, 93.0%, and 97.3%, and by 63.1%, 91.5%, and 98.5% at a nanoparticle dosage of 1%, 3%, and 5%, respectively (Fig. 4a). Similarly, the TCLP leachable Cu and Zn concentrations were decreased by 27.9%, 48.8%, and 62.8%, and by 1.8%, 22.9%, and 27.0%, respectively (Fig. 4b).

The key technical obstacles with this technology are the deliverability of the particles, reaction rate, and the long-term effectiveness. Typically, powder or particulate phosphate minerals or aggregated nanoparticles are added to soil through off situ mixing, and thus are suitable for shallow soil that is polluted with high concentrations of heavy metals. While the reaction rate is often slow and is limited by the desorption rate of the target metals from the soil, the phosphate minerals may offer prolonged effectiveness and may provide a permanent sink for the metals. In contrast, soluble phosphate may be easily injected into the target soil and provide faster reaction with the target metals and reach the metals in deeper soil. However, soluble phosphate may only offer shorter reaction lifetime and most phosphate may be unused and washed into the downstream, which may cause secondary contamination issues (Liu and Zhao, 2007). Liu and Zhao (2007, 2013) developed a new class of stabilized phosphate nanoparticles (carboxymethyl cellulose (CMC) stabilized iron phosphate and CMC stabilized Caphosphate). The stabilized nanoparticles can be delivered into moderately permeable soil and facilitate in situ remediation. The nanoparticles not only offer much improved binding rate and

capacity, but also well controlled transport in the subsurface, i.e., their mobility can be controlled by manipulating external injection pressure (He et al., 2009). Once delivered, the nanoparticles will remain in the confined domain without spreading as soluble phosphates do.

Phosphate based amending agents are of particular interest to remediation of agricultural soil. Not only are these materials innocuous to the crops, they may also serve as slow-releasing fertilizers, while binding with the target heavy metals. Yet, more field data are needed to gauge the long-term effectiveness and assess the associated impacts on the crops and the local environment.

3.2.1.3. Liming materials. Common liming materials include oyster shells and eggshells (Lim et al., 2013), lime, and limestone (He et al., 2016). For their affordable price and ready availability, liming materials have been widely accepted as a low cost and effective amendment in reducing the toxicity of heavy metals in field applications. Soil liming enhances sorption and/or precipitation of heavy metals by increasing soluble pH and increasing the negative surface potential of soil matrices.

Cui et al. (2016a) reported that lime amendment effectively decreased the leachability (TCLP and synthetic precipitation leaching procedure (SPLP)), availability (CaCl₂ and MaCl₂), and bioaccessibility (simplified bioaccessibility extraction test (SBET)) of Cu and Cd in a contaminated soil in Guixi City, Jiangxi Province, China. For instance, the TCLP extractable Cu concentration was decreased by 7.90 mg/L compared with control and the SBET extractable Cu was reduced from 6.09 mg/L (control) to 4.65 mg/L. Hong et al. (2009) evaluated the uptake of Cd and Zn by radish (Raphanus sativa L.) after the application of Ca(OH)₂ at 0, 2, 4, and 8 mg/ha, and found that both plant-sorbed and NH₄OAc extractable Cd and Zn concentrations were progressively decreased with increasing Ca(OH)₂ dosage due to the increase in CEC and pH of soil. Lim et al. (2013) investigated immobilization of Cd and Pb in soil using oyster shells and eggshells. After 420 d of incubation, the exchangeable fraction of Cd evolved from 23.64% to 1.90-3.81%, while the carbonate fraction increased from 19.59% to 36.66–46.36%. Similar trend was also observed for Pb. In addition, the treatment also effectively reduced the TCLP leachable Cd and Pb.

Liming materials are often used as co-amendments to enhance the sequestration of heavy metals in soil remediation. Wu et al. (2016) combined limestone and sepiolite to remediate a Pb– and Cd-contaminated paddy soil near a mining area in southern Hunan, China. They found that the amendment increased the soil pH by up to 1.95 units and decreased the exchangeable concentrations of Pb and Cd by up to 99.8%.

Like the case of soluble phosphates, the use of soluble lime has the advantage of rapid reaction rate, but only limited reactive lifetime as the solution may be washed away rapidly by rainwater or along with flowing groundwater. In addition, immobilization through merely formation of metal oxides or hydroxides may be less durable and may subject to re-dissolution when the ambient pH is re-established.

3.2.1.4. Organic composts. Organic composts include biosolids and animal manure. Biosolids are solid residues generated during primary, secondary, or advanced treatments of domestic sanitary sewage. Conventionally, biosolids applied to land are viewed as one of the major components for metal accumulation in soil. Advances in the treatment of sewage wastewater and separation of industrial wastewater in the sewage treatment plants have resulted in a steady decline in the metal contents of biosolids. Alkaline stabilized biosolid composts have been used as an effective sink for reducing the bioavailability of metals in contaminated soil and sediment. Basta et al. (2001) demonstrated that lime-stabilized biosolid greatly reduced the phytoavailability of Cd and Zn at smelter sites in Oklahoma. Placek et al. (2016) applied sewage sludge as an additive to soil contaminated with Cd, Zn, and Pb in a field study. The application of sewage sludge increased the soil pH, CEC, and content of humic acids, leading to an improved metal sorption capacity. As a result, the readily soluble forms of the metals and the leaching of biogenic components were reduced.

Animal manure is another major source of valuable organic amendments. The principal sources of manure are from chicken, swine, beef cattle, dairy, and poultry wastes. Most manure products contain low levels of heavy metals though high concentrations of Cu and Zn have been found in swine manure and As in poultry litter. Recent advances in the treatment of manure byproducts have resulted in reduced bioavailability of metals in animal manure. For example, 87% reduction in Cu and Zn in wastewater from swine houses was obtained after treatment with lime slurry, ferric chloride, or polymer (Westerman and Bicudo, 2000). Similarly, treatment of poultry manure with alum $[Al_2(SO_4)_3]$ decreased the concentration of water-soluble As, Zn, Cu, and Cd (Moore et al., 1998). Hence, land applications of livestock and poultry manure byproducts are generally based on total N and P loadings, while allowable trace element loadings are often the limiting factors for other biosolids.

Manure byproducts with low contents of metals can be used as a sink for immobilizing heavy metals in soil, especially for agricultural soil because of the rich nutrients. Li et al. (2016) investigated the fractionation of Cd, soil biological properties, and Cd uptake by wheat following a chicken manure compost amendment in a Cd-contaminated field soil. They found that the compost increased soil pH, total P content, and SOM content, and enhanced soil biological properties such as microbial biomass, invertase, protease, urease and catalase activities by up to 3.5 times. Moreover, the treatment decreased the acid-extractable Cd by 8.2–37.6%, and increased the reducible and oxidizable Cd by 9.2–39.5% and 8.2–60.4%, respectively.

Organic amendments usually contain cellulose and lignin as the main constituents. Other components are extractives, hemicellulose, proteins, lipids, starches, simple sugars, hydrocarbons, and many other compounds that contain a number of functional groups such as carbonyl, phenolic, acetamido groups, amido, amino, structural polysaccharides and esters, which can bind with various transition metals (Niazi et al., 2016). In addition, application of organic amendments also leads to elevated soil pH, which is conducive to metal immobilization due to formation of metal hydroxides and/or by preventing sulfide oxidation/hydrolysis (Walker et al., 2004) as well as increased negative surface potential (Gadd, 2000). Organic amendments are particularly attractive to remediating agricultural soil for their 'greenness" and multitude of beneficial side effects on soil fertility. Moreover, the increase of organic matter by organic amendments can lead to decrease of soil bulk density and increase of soil aeration due to the redistribution of soil pore space (Tejada et al., 2006).

3.2.1.5. Metal oxides. Metal oxides, such as oxides of Fe, Mn, and Al, with large active surface areas and the amphoteric nature have been extensively studied as metal stabilizing amendments in contaminated soil. These mineral components can strongly bind metals via specific sorption, co-precipitation, and inner-sphere complexation. Their application is aimed to decrease the mobile, bioavailable, and bioaccessible fractions of metals in soil, and thus minimizing leaching from soil and uptake by soil organisms, plants, crops, and humans.

Field tests have demonstrated the effectiveness of iron oxides (e.g., hematite, maghemite, and magnetite) and oxyhydroxides (e.g., ferrihydrite, goethite, akaganeite, lepidocrocite, and feroxvhite) for immobilization of various heavy metals and metalloids (e.g., Sb, Pb, and As). Iron oxides were applied to immobilize As in a paddy field soil near an abandoned Au–Ag mine in Korea, and the amendment effectively prevented As transfer from soil to pore water and crops (Ko et al., 2015). Okkenhaug et al. (2016) investigated the mobility, distribution, and speciation of Sb and Pb in a shooting range soil in South Noway when treated with ferric oxyhydroxide powder (CFH-12) (2%) coupled with limestone (1%). The treatment resulted in an average decrease of Sb and Pb in pore water by 66% and 97%, respectively, which remained stable over four years. Leachable Sb and Pb were transformed to amorphous iron oxides bound or even more crystalline and residual mineral phases.

Increasing iron oxides contents in soil can be practically achieved through the application of their precursors, e.g., iron sulfates, and elemental iron (Hartley and Lepp, 2008). Warren and Alloway (2003) reported that application of 1.89% (w/w) of commercial grade FeSO₄ resulted in 0.54% of iron oxides in treated soil. However, soil acidification has been cited as one of the side effects associated with this practice:

$$4FeSO_4 + O_2 + 6H_2O \rightarrow 4FeOOH + 4SO_4^{2-} + 8H^+$$
(3)

As the acidification could cause remobilization of metallic cations, lime is often co-applied to control the soil pH. However, addition of bicarbonate alkalinity, which is commonly practiced in water coagulation, should be avoided as bicarbonate is a fairly strong ligand and may complex and mobilize transition metals (Lewis acids). The use of waste elemental iron as a precursor of iron oxides in soil has been shown to be a potentially effective and cheap amendment for decreasing the mobility and potential bioavailability of various metals in contaminated soil. Under field conditions, elemental iron is oxidized to FeOOH via (Liu et al., 2014):

$$4Fe + 3O_2 + 2H_2O \rightarrow 4FeOOH \tag{4}$$

The surface oxide layer provides active sites for complexation of heavy metals (Huang et al., 2016). Xie et al. (2016) injected dissolved Fe(II) and NaClO into the As-contaminated aquifer in the field to promote the formation of Fe oxides/hydroxides, which can effectively oxidize As(III) into As(V), and thus removed aqueous both As(III) and As(V) via adsorption, co-precipitation and/or incorporation of As(V) oxyanions into goethite.

Of the various forms of manganese oxides (birnessite,

todorokite, cryptomelane, and hausmannite), birnessite ([Na,Ca,K]_xMn₂O₄·1.5H₂O), also known as δ -MnO₂, is the most common Mn oxide. Due to the large specific surface area and low pH of point of zero charge (pH_{PZC}) (1.8–4.5) (Dong et al., 2000; Feng et al., 2007), it is much more efficient in adsorbing some metals especially Pb compared to Fe oxides. Equations (5) and (6) depict the adsorption of divalent metals (Me²⁺) onto the amphoteric surface groups of Mn oxides (Zaman et al., 2009):

$$\equiv MnOH + Me^{2+} \rightarrow \equiv MnOMe^{+} + H^{+}$$
(5)

$$\equiv 2MnOH + Me^{2+} \rightarrow \equiv (MnO)_2Me + 2H^+ \tag{6}$$

McCann et al. (2015) applied a natural Mn oxide at a dosage of 10% to immobilize Pb in a historically Pb-contaminated soil. The material demonstrated a maximum Pb adsorption capacity of 346 mg/g, and had no adverse effect on soil microbial functioning. In addition to adsorption, δ -MnO₂ offers remarkable oxidizing potential, which can effectively convert As(III) to As(V) (An and Zhao, 2012) and degrade organic contaminants such as steroids and antibiotics (Han et al., 2015).

As of soil delivery, most metal oxides can only be added into soil in the form of powder or granular particles through mechanical mixing, which largely impedes their application to deeper soil or in situ remediation uses. When soluble precursors are added, the effectiveness is then limited by the shorter retention time and the lack of mixing in the subsurface. To overcome these practical issues, stabilized metal oxide nanoparticles such as magnetite and Fe-Mn binary oxide are promising for metal immobilization due to their large specific surface area, high reactivity, and controllable transport in soil (An and Zhao, 2012; Liang and Zhao, 2014; Xie et al., 2015). For instance, An and Zhao (2012) investigated the immobilization of As(III) in soil using Fe-Mn binary oxide nanoparticles with CMC as a stabilizer. The water leachable arsenic and the TCLP leachability were reduced by 91-96% and 94-98%, respectively, at an Fe-to-As molar ratio of 6.5–39. The nanoparticles demonstrated good soil deliverability and column elution tests of the contaminated soil showed that the nanoparticles transferred nearly all water-soluble As(III) to the nanoparticle phase. The nanoparticle amendment reduced the TCLP leachability of As(III) remaining in the soil bed by 78%.

3.2.1.6. Biochar. Biochar is a carbon rich and porous charcoal manufactured during the pyrolysis of organic residues such as municipal waste, animal wastes, wood, crop residues, and biosolids. Recent studies have demonstrated that biochar is able to immobilize soil heavy metals and metalloids and reduce their accumulation in plants, which is often attributed to biochar's highly porous structure, active functional groups, elevated pH, and decent CEC (Beesley et al., 2011; Vithanage et al., 2017; Zhang et al., 2013). In addition, land application of biochar has been cited to improve chemical, physical, and biological properties of soil.

A number of field tests have been reported in investigating the effectiveness of biochar for soil remediation, and Table 2 summarizes these latest technologies. Bian et al. (2014) conducted a threeyear field remediation study (2010–2012) in a Cd and Pb contaminated rice paddy in southern China, where bioavailable Cd and Pb in the soil were monitored after a single soil amendment of wheat straw biochar at a dosage of 40 t/ha. The amendment consistently and significantly increased soil pH and total organic carbon, and decreased CaCl₂ extractable Cd by up to 70.9% and Pb by up to 79.6% over the three year period. As a result, the total Cd uptake by rice (*O. sativa* L.) was reduced by up to 67.3%, and the total Pb uptake was decreased by up to 69.0%. Meanwhile, the rice yield was increased by 18.3% in the third year. Biochar amendment was found to alter the binding or speciation of Cd and Pb in soil. Cui et al. (2016b) reported that biochar transformed the exchangeable fractions of Cd and Pb into relatively more stable fractions (residual and organic). For instance, the exchangeable fractions of Cd and Pb were decreased by 8.0-44.6% and 14.2-50.3%, and the residual fractions were increased by 4.0-32.4% (Cd) and 14.9-39.6% (Pb) during five vears. The added affinity of heavy metals was attributed to the abundant functional groups and complex structures of biochar. The contamination of Cd and As in paddy soils is a serious concern in southern China. However, simultaneous immobilization of these co-contaminants is hindered by the different geochemical behaviors of Cd and As in paddy fields. While application of biochar effectively immobilized Cd, it also facilitated As(V) reduction into As(III), resulting in increased As toxicity and leachability in the contaminated fields (Chen et al., 2016b; Vithanage et al., 2017). Yu et al. (2018) developed a zero valent iron (ZVI)-biochar composite for simultaneous immobilization of Cd and As in two paddy fields in Guangdong Province, China, from 2013 to 2015. The corrosion products of ZVI demonstrated high sorption capacity for As and biochar showed high capacity for Cd. When applied at 2250 kg/acre on a rice field, the treatment reduced the accumulation of Cd and As in rice by 48% and 24%, respectively.

Increasing the biochar dosage enhances the immobilization effectiveness. Housen et al. (2013) investigated the effect of different application rates of biochar (1%, 5%, and 10%) on the fate of Cd, Zn, and Pb in a contaminated soil in Belgium, and reported that the CaCl₂ exchangeable fraction of metals in soil was decreased with increasing rates of biochar after 56 days of incubation.

Long-term effectiveness and performance are important criteria to evaluate heavy metals remediation technologies. Shen et al. (2016) conducted a field remediation treatment to examine the "long-term" effect of biochar on the immobilization of heavy metals at a contaminated site (soil pH = 8) in Castleford, UK. Following the application of biochar at 0.5-2%, the Ni and Zn concentrations in the carbonic acid leaching tests were reduced by 83-98% over three years. The biochar amendment enhanced the residual fraction of Ni and Zn in the soil from 51% to 61-66% and from 7% to 27-35%, respectively. However, the field trials conducted by Cui et al. (2016a) showed that the effectiveness of the biochar decreased over time and repeated application was required for full effectiveness. They observed a decrease in soil pH and an increase in bioavailability of Cu and Cd due to leaching of alkalinity.

Biochar has the advantage over organic composts of having a stable fixed carbon structure and a typically high alkalinity. Biochar amendment makes for a "multiple-win" scenario, including carbon sequestration, soil improvement (i.e., enhanced soil capacity for retaining nutrients and water, and improved soil mechanical strength), agronomic benefits, metal immobilization, and reuse of solid waste. However, like the case of clay minerals, the application of biochar are restricted by the limited adsorption capacity and affinity, soil deliverability and reaction rate, and are only suitable for shallow soil contaminated with heavy metals. There is also limited information available on the long-term stability of metals immobilized at the field scale. In addition, the biochar's effectiveness depends on various factors including metal type, immobilization time, site-specific factors (e.g., climate, biochar dosage, and mixing depth), biochar feedstock type, and biochar properties.

3.2.2. Solidification/stabilization

Solidification/stabilization (S/S), also referred to as waste fixation, has been widely adopted to amend heavy metals contaminated soil due to its relatively low cost and easy implementation. Soil solidification is a process that encapsulates the waste materials in a monolithic solid of high structural integrity (Khan et al., 2004). In contrast, soil stabilization refers to a process of amending contaminated soil with chemical reagents to convert leachable chemicals to physically and chemically more stable forms. It often involves chemical interactions between the target heavy metals and the binding agents (Chen et al., 2009). The objectives of S/S are to achieve and maintain the desired physical properties and to chemically stabilize or permanently sequestrate contaminants in the solid phase, thereby preventing the chemicals from harming the environment or biota.

A good binder plays a decisive role in the remediation effectiveness of S/S processes. Cement-based binders are commonly used for implementation of S/S technologies in the field. A field study conducted by Wang et al. (2014a) demonstrated excellent efficacy of cement-based binders in remediating metalscontaminated soil at a site in West Drayton. After 17 years of the remediation, the TCLP-leachable concentrations of Cu, Ni, Zn, Pb, and Cd remained below the Private Water Supplies Regulations (England) 2009. Antemir et al. (2010) evaluated the field performance of cement-based S/S techniques at a former fireworks and low explosives manufacturing site in England after four years of operation. The results indicated that the treated soil was progressively carbonated over time and that Pb, Zn, and Cu were adequately immobilized.

Calcium aluminate cement (CAC) has received increasing attention as an alternative binder. Navarro-Blasco et al. (2013) studied the adsorption capacities of CAC for Pb, Zn, and Cu, and found that the total uptake could reach up to 3 wt%. Voglar and Lestan (2013) used CAC and sulfate resistant Portland cement (SRC) as binders for immobilizing Zn, Pb, Cu, As, Cd, and Ni in soil at a brownfield site in Slovenia. They reported that the CAC treatment produced S/S soil monoliths of higher mechanical strength (up to 7.65 N/mm²), and reduced the leachability of Zn, Pb, Cu, As, Cd and Ni more effectively than SRC.

Blending novel binders and additives (e.g., magnesia and zeolites) with the conventional binders is expected to provide added benefits due to their individual credentials in improving the overall S/S effectiveness. Wang et al. (2015) evaluated the performance of various binders including Portland cement (PC), ground granulated blast furnace slag (GGBS), pulverized fuel ash (PFA), MgO, and zeolite for *in situ* S/S field trials at a site contaminated with complex heavy metals (e.g. Pb, Zn, Cr, Cu, and Ni) and organic chemicals in the UK. S/ S was implemented using a triple auger system, where soil was mixed to a depth of 4 m. At various contaminant and binder levels, unconfined compressive strength (UCS) values were 22-3476 kPa, and the leachability of the heavy metals in contaminated soil was in the range of 0.002-0.225 mg/L based on the batch leaching procedures of BS EN 12457-2. The combination of GGBS and MgO at a ratio of 9:1 demonstrated a higher material strength and better immobilization efficiency for heavy metals. Wang et al. (2016) further evaluated the physical and chemical performance of MgObearing binders for immobilizing heavy metals in contaminated soil over three years after the treatment. The results showed that MgO-GGBS blends provided higher strength and less leachability of heavy metals compared to PC or MgO alone.

S/S has been considered as one of the most efficient and low-risk remediation methods. It has several main advantages including relatively low cost, easy to implement, enhanced soil comprehensive strength, high resistance to biodegradation, and broad engineering applicability. However, the metals are not removed from soil, and further long-term monitoring of heavy metals on site are required. The longevity of the S/S materials is also questionable. Moreover, this technology usually results in a volume increase in treated media.

3.2.3. Soil washing

Soil washing refers to leaching of heavy metals from soil matrix

with various reagents or extractants, such as water, inorganic acids, organic acids, chelating agents, and surfactants. Typically, contaminated soil is dug out and mixed with a suitable extractant solution for a specified time depending on the type of metals and soil. The extractant can transfer heavy metals from soil to the liquid phase via chemical dissolution, ion exchange, chelation or desorption (Ferraro et al., 2015). The treated soil, upon regulatory permission, is then backfilled to the original sites. Barring the cost, soil washing permanently removes metal contaminants from soil, and is a rapid method that can fulfill the remediation goals without any long-term liability (Park and Son, 2017).

A variety of chelators have been tested for soil washing at the field scale. EDTA is the most frequently reported chelating agent due to its strong chelating ability for various heavy metals. Hu et al. (2014) assessed the metal removal efficiency of EDTA from soil contaminated with Cd, Cu, Pb, and Zn. The on-site metal removal efficiencies were determined to be 80%, 69%, 73% and 62% for Cd, Cu, Pb and Zn, respectively. However, there is a growing environmental concern about EDTA washing because of its poor biodegradability and high persistence in the soil environment, which might result in deterioration of soil functions. Wang et al. (2018) employed four biodegradable chelators, namely, iminodisuccinic acid (ISA), glutamate-N,N-diacetic acid (GLDA), glucomonocarbonic acid (GCA), and polyaspartic acid (PASP), for extracting heavy metals from field-contaminated soils collected at a lead-zinc contaminated mining wasteland and from a farmland near a nonferrous metal smelter in China. The removal of Cd. Pb. and Zn reached 45%, 53%, and 32%, respectively, for the mining soil and 85%. 55%. and 64% for the farmland soil. Moreover, the leachability. mobility, and bioaccessibility of the residual metals after the washing processes were decreased notably compared to the original soil.

Other washing chemicals include salt and high concentrations of chloride solution, such as calcium chloride and iron(III) chloride (Guo et al., 2016). Nagai et al. (2012) showed that on-site soil washing with FeCl₃ was able to effectively remove Cd in paddy soil. The acid-soluble Cd concentrations in the washed soil extracted with 0.1 M HCl decreased by 47% compared to the untreated soil. Phosphate solutions can be applied to specifically extract arsenate from soils due to their structural similarity (i.e., tetrahedral oxyanions) of phosphate ions (PO³₄⁻) and arsenate ions (ASO³₄⁻). Jho et al. (2015) reported that soil washing with a 0.5 M phosphate solution for 2 h removed 24.5% of As from an As-contaminated soil at a former smelter site.

Soil washing is one of the few permanent treatment alternatives to remove heavy metals or metalloids from soil. It is rapid, highly effective, and may allow recovery of the metals in certain cases. It markedly reduces the volume of treated soil, and the processed soil may be returned to the site. However, for field scale applications, this technology bears with several disadvantages: (1) the treated soil may be inappropriate for revegetation due to the deterioration of soil properties and the loss of nutrients and SOM; (2) the presence of chemical agents in the treated soil may cause potential adverse effects; (3) the wastewater produced must be further handled or treated, which can be quite costly; and (4) it only removes the extractable fractions of the contaminants, and the degree of removal depends on the chemical agents used. Development of low-cost and 'green' flushing extractants will help to address these concerns.

3.3. Biological remediation

Biological remediation is one of the most environmentally friendly options to rectify and re-establish the natural conditions of contaminated soil. It makes use of microorganisms/plants, nonviable or viable, natural or genetically engineered, to detoxify or remove heavy metals from the soil and to improve soil quality and restore soil function (Ye et al. 2017a, 2017b). While it may take a long remediation time, it is usually rather cost effective and noninvasive, and may be used to enhance natural attenuation processes.

3.3.1. Phytoremediation

Phytoremediation is a technology that utilizes specialty living plants to fix or adsorb contaminants, to remove the contaminants from soil or reduce their environmental impacts, and thereby, remediating and revegetating contaminated soil. It is considered to be an environment friendly, attractive, aesthetically pleasant, non-invasive, energy efficient, and cost-effective technology to clean up sites with low to moderate levels of heavy metals. The modern technologies of phytoremediation are based on different uptake mechanisms, which include phytostabilization, phytoextraction, and phytovolatilization (Fig. 1).

Phytostabilization or phytoimmobilization is the use of plants with ability to decrease the mobility or/and bioavailability of contaminants via certain mechanisms including adsorption by roots, chemical precipitation, and complexation in the root zone. To this end, long-living plants such as poplar trees are often employed. Cheng et al. (2016) investigated the feasibility of phytoremediation using *Miscanthus floridulus* with high dry matter yields and a strong vitality on a fallow land contaminated with high concentrations of lead (up to 6000 mg/kg). After one year, the lead content in the roots reached 806.7 mg/kg, and the plant immobilized 1.13 kg/ha/ year of lead from the soil. It should be noted that phytostabilization is only effective for a limited depth to the extent the roots can reach, and the heavy metals remain in the soil or plants, which may need to be monitored regularly or further treated.

Phytoextraction, also known as phytoaccumulation, phytoabsorption, or phytosequestration, refers to the uptake of contaminants from soil by plant roots and their translocation and accumulation in the aboveground biomass, i.e., shoots. Metal translocation to shoots is a crucial biochemical process desirable for effective phytoextraction since the harvest of the root biomass is generally not feasible. Yang et al. (2017) conducted a field study to evaluate the heavy metal phytoextraction potential of the Ashyperaccumulator *Pteris vittata* L. and the castor bean (*Ricinus communis* L.) in a co-planting system, where soil was contaminated with As, Cd, and Pb. They showed that the co-planting significantly increased the yield of *P. vittata* and the uptake of As and Pb by *P. vittata*. The addition of water-soluble chitosan further enhanced the uptake of Cd and Pb by *P. vittata* and *R. communis*.

Phytovolatilization is an approach that involves the uptake and transpiration of metals into their volatile forms and their release into the atmosphere through stomata. This technique is primarily useful for Hg, where mercuric ions are transformed into relatively less toxic elemental form. Because the volatile form of Hg released into the atmosphere may be recycled back to the soil by precipitation, this technique presents a temporary solution of the problem. In practice, phytovolatilization of mercury is considered as a natural consequence of the interaction between plant species with mercury in soil. Leonard et al. (1998) studied mercury exchange flux between aerial parts of five plant species (Lepidium latifolium, Artemisia douglasiana, Caulanthus sp., Fragaria vesca, Eucalyptus globulus) grown on a Hg-contaminated soil (450-1605 mg/kg) and air in a glasshouse at 30 ± 5 °C. In the daytime, the plant-toatmosphere emission of mercury was in the range of 10-93 ng/ m^2/h , and *Caulanthus* sp. demonstrated the highest mercury emission rate. For all the plant species, emissions in the dark were an order of magnitude less than that during the daytime. Mercury volatilization through the stomata accounted for ~90% of the total mercury emission.

Phytoremediation has been considered to be an attractive option for remediation of soil with low to moderate levels of metal pollution. However, it typically takes a lengthy remediation period. The efficiency is generally restricted by the low biomass and slow growth rate of metal hyperaccumulator plants, and the metalsenriched biomass may need further handling and disposal. Moreover, some hyper-accumulating species may be invasive, and thus subject to regulatory restrictions. Lastly, sustainable phytoremediation depends on the climatic and weather conditions.

3.3.2. Microbial remediation

Microbial remediation refers to the process of using microorganisms (i.e., bacteria, fungi, and algae) to induce the adsorption, precipitation, oxidation, and reduction of heavy metals or metalloids in soil, thereby lowering the availabilities of the contaminants. The microorganisms may be indigenous to a contaminated area or may be isolated from elsewhere. In practice, contaminated soil is inoculated with selected microorganisms by spray irrigation or infiltration galleries. Injection wells may be applied if the contaminants are deep in soil. Typical microbial remediation techniques include biosorption, bioprecipitation, bioleaching, biotransformation, and biovolatilization.

Biosorption is a process that involves trapping of heavy metals via the cellular structure of a microorganism and subsequently sorption onto the binding sites of the cell wall. The microbial cell wall, consisting of polysaccharides, lipids, and proteins, offers many functional groups including carboxylate, hydroxyl, amino and phosphate groups that can bind heavy metals. Extracellular polymeric substances (EPS) or exopolysaccharides secreted by microorganisms have been reported to act as surface active agents for binding with heavy metals. Wang et al. (2014b) applied a mutant species (B38) from the wild type of *Bacillus subtilis* under UV irradiation together with a bio-fertilizer *NovoGro* (NG) for remediation of farmland soil contaminated with Cd, Cr, Hg, and Pb in Tianjin, China. They demonstrated that B38 was an effective biosorbent for the heavy metals, and the co-amendment of B38 and NG reduced the heavy metal contents in the edible part of radish by 30.8–96.0%.

Bioprecipitation describes the transformation of soluble species of heavy metals or metalloids into insoluble hydroxides, carbonates, phosphates, and sulfides through microbial metabolism. Researchers have reported the role of sulfate reducing bacteria (SRB) in immobilizing heavy metals by generating sulfides (Vitor et al., 2015; Zhang and Wang, 2016). Groudev et al. (2014) investigated the effect of SRB biostimulation on the mobility of Cd, Cu and Zn from an acidic leached cinnamonic forest soil under field conditions, and found that the metals were precipitated as the insoluble sulfides as a result of the activity of the indigenous SRB inhabiting in the soil subhorizon (30–50 cm).

Bioleaching refers to the dissolution of metallic minerals and the release of associated metals via microorganism activity. The microorganisms used mainly include chemoautotrophic bacteria and fungi, such as *Leptospirillum ferrooxidans*, *Acidithiobacillus thiooxidans*, *Acidithiobacillus ferrooxidans*, and *Aspergillus niger*. The well-known Fe/S-oxidizing bacteria *Thiobacillus* and *Leptospirillum ferrooxidans* can oxidize iron and sulfide, producing sulfuric acid and releasing associated heavy metals (Akcil et al., 2015). Nguyen and Lee (2015) found that As, Cu, Fe, Mn, and Zn were removed by 42.4%, 45.0%, 47.7%, 92.%, and 67.2%, respectively, in mine tailings using a mixed culture of *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans*, after 500 h at 0.5% elemental sulfur concentration. Zeng et al. (2015) reported that *Aspergillus niger* strain SY1 effectively removed Pb, Cd, Cu, and Zn from contaminated sediment by up to 99.5%, 56.0%, 71.9%, and 76.4%.

Biotransformation (e.g., methylation/reduction and

dealkylation/oxidation) can change the chemical form of heavy metals, and thus altering their mobility, toxicity, and bioavailability. It is particularly applicable to heavy metals whose toxicity varies with different oxidation states. For instance, the mercury-resistant bacteria Organomercurial lyase converts methyl mercury to Hg(II), which is one hundred-fold less toxic than methyl mercury (Wu et al., 2010). Direct enzymatic reduction through metal-reducing microorganism can reduce soluble and mobile Cr(VI) into insoluble and immobile Cr(III) (Jobby et al., 2018). Tapase and Kodam (2018) isolated an arsenic oxidizing α -proteobacterial strain Microvirga indica S-MI1b sp. nov. from a heavy metal contaminated soil and found that the strain possessed arsenite oxidase gene and completely oxidized 15 mM As(III) to As(V) within 39 h. This approach may be extended to immobilization of many other redox active contaminants such as Se, U, and Tc. However, cautions should be exercised to avoid converting less mobile or less toxic forms of metals or metalloids into more mobile or more toxic forms.

Biovolatilization involves turning a soluble contaminant into its volatile state. For metals or metalloids, this technique is only applicable to Se and Hg (Wu et al., 2010; Chen et al., 2018; Tan et al., 2016). For instance, mercury-resistant bacteria can utilize the MerA enzyme to reduce Hg(II) to the volatile form Hg(0) (Wu et al., 2010). Chen et al. (2018) tested a two-stage system (chemical extraction followed by microbial reduction) for removal of Hg from field-contaminated soils. They found that ~77% of Hg was extracted from the soils after the first-step extraction process with 0.5 M ammonium thiosulfate, and up to 81% of Hg²⁺ was transformed from the washing solution through the biotransformation of Hg-reducing bacteria *Enterobacter cloacae*.

Microbial remediation has been considered as a safe, easy, and effective technology. It has the advantages of low energy requirement, low operation cost, no environmental and health hazards, and possibility of recovering heavy metals. It is a natural process, and is therefore perceived by the public as an acceptable treatment process. Yet, microbial remediation is effective only when environmental conditions permit the desired microbial growth and activity. Additional nutrients, oxygen, and other amendments are usually required to stimulate microbial activity and enhance the bioremediation process. The process is usually slow and time consuming, and it is often needed to combine bioremediation with physical-chemical approaches to speed up the remediation process and boost the efficiency.

3.3.3. Microbial assisted phytoremediation

The rhizosphere is an important habitat for microorganisms, including bacteria, fungi, algae, and protozoa. The efficiency of phytoremediation can be enhanced by assistance of plant growth promoting (PGP) bacteria, including *Serratia*, *Bacillus*, *Pseudomonas*, *Burkholderia*, *Enterobacter*, *Erwinia*, *Klebsiella*, *Beijerinckia*, *Flavobacterium*, and *Gluconacetobacter* (Babu et al., 2013; Sheng et al., 2008; Tak et al., 2013).

The enhancement can be achieved in several ways. First, these bacteria have the ability to affect heavy metals mobility and availability to the plant, and they can transform heavy metals into bioavailable and soluble forms through the action of siderophores, organic acids, biosurfactants, biomethylation, and redox processes, facilitating plant uptake of the soil-bound metals. The bacteria have developed various metal tolerance mechanisms including exclusion, biosorption, active removal, precipitation or bioaccumulation in both external and intracellular spaces (Rajkumar et al., 2009). In addition, enzymatic detoxification represents another metal-resistance mechanism, e.g., bio-reduction of Hg(II) into Hg(0). Second, PGP bacteria possess several growth-promoting capabilities, including phosphorus solubilization, nitrogen fixation, iron sequestration, and phytohormone and ACC (1-aminocyclopropane-

1-carboxylic acid) deaminase synthesis (Li and Ramakrishna, 2011), which can improve plant growth, increase plant biomass, and in turn assist phytoremediation. For instance, Jiang et al. (2008) isolated a heavy metal-resistant bacterial strain identified as Burkholderia sp. J62 from a heavy metal contaminated soil, and applied to a field contaminated soil with Pb and Cd. The isolate increased bacterial solubilization of both metals in both solution culture and in soil, with production of indole acetic acid, siderophore and 1aminocyclopropane-1-carboxylate deaminase, and also dissolution of inorganic phosphate. Moreover, the treatment significantly improved the biomass of maize and tomato plants, and enhanced the accumulation of Pb and Cu in the plant tissues. Babu et al. (2013) reported that inoculating soil with the bacterial strain isolated from roots of Pinus sylvestris significantly increased biomass, chlorophyll content, nodule number, and accumulation of heavy metals (As, Cu, Pb, Ni, and Zn) in the hyperaccumulator *Alnus firma*. seedlings.

3.4. Combined remediation

Combined remediation involves applications of two or more physical, chemical, and/or biological remediation technologies. It supplements the limitations with individual technology alone, and takes advantage of different techniques to enhance the remediation efficiency. Combined remediation methods, such as chemically assisted phytoextraction (Wang et al., 2011), electrokinetic remediation coupled with complexing agents (Robles et al., 2012), electrokinetic remediation combined with phytoextraction (Mao et al., 2016), citric acid facilitated thermal treatment (Ma et al., 2015), soil washing coupled with chemical stabilization (Zhai et al., 2018), chemical stabilization and phytoremediation (Fellet et al., 2014) have attracted a lot of attention. For instance, Wang et al. (2011) investigated mercury uptake by plant Chenopodium glaucum L. growing on a mercury-contaminated soil, and observed that addition of ammonium thiosulphate (a sulfur-containing ligand) significantly increased the solubility of mercury, and thereby enhanced the mercury uptake. Robles et al. (2012) demonstrated that complexing agents such as EDTA can facilitate mercury removal from mining soils in Querétaro, Mexico, in an electrokinetic remediation process. Up to 75% of Hg was removed by wetting the soil with 0.1 M EDTA and after 6 h of electrokinetic treatment. The enhanced efficacy was attributed to increased electromigration of the EDTA-Hg complexes. Ma et al. (2015) combined citric acid and thermal treatment to enhance Hg removal from a farmland soil in Guizhou Province, China. At a citric acid/Hg molar ratio of 15, the mercury level in soil was reduced from 134 to 1.1 mg/kg upon treatment at 400 °C for 1 h, with an estimated reduction of energy input by 35%. The addition of citric acid enhanced the volatilization of mercury by providing an acidic environmental condition. Wu et al. (2017) reported that combining biochar amendment and composting is an attractive remediation technology. The interaction of biochar and composts boosted the nutrients, CEC, functional groups, and organic matter on the biochar, and increased the nutrients, CEC, organic matter, and microbial activities of the composts. These favorable modifications are expected to improve the efficiencies for soil amendment and remediation.

4. Economic considerations

Physical remediation methods generally require large amounts of manpower and material resources, whereas chemical approaches require a larger cost share for chemicals or reagents. In general, chemical approaches are more cost-effective than physical remediation under similar remediation goals, especially for deeper soil and where only low dosages of immobilizing agents or chemical extractants are needed. Bioremediation is more economical and greener than physical/chemical approaches, but its uses are confined by the reachability of biota and technical effectiveness. US EPA (2004) reported that the total for phytoremediation ranged from US \$25 to \$100 per ton of soil, compared to \$300-\$500/ton for vitrification and \$75-\$210/ton for soil washing. FRTR (2007) reported a cost range of \$50-\$117/m³ for electrokinetic remediation and \$33-\$32/m³ for soil washing. Martin and Ruby (2004) estimated a cost of \$40-\$65/m³ for *in situ* chemical stabilization. Chang and Yen (2006) estimated a cost of US \$834/m³ for a full-scale thermal desorption process (750 °C for 3 h) to treat mercurycontaminated soil.

5. Concluding remarks and future research needs

Soil contamination by heavy metals has been a worldwide challenge, and remediation technologies have come a long way over the past decade or so. This review presents the latest development and knowledge on the general principles and effectiveness of key remediation techniques that have been studied or demonstrated at the field scale. In general, physical remediation methods can remove heavy metals/metalloids from contaminated soil/ groundwater, eliminating long-term effects, and are effective for highly contaminated sites with multiple heavy metals/metalloids. However, these methods are highly costly, environmentally destructive, and only applicable to small contaminated volume where the contaminants are readily accessible. Chemical methods are rapid, simple, easy-to-apply, relatively economical, and may be used for in situ remediation. However, chemical stabilization techniques do not remove the contaminants from the media, and long-term monitoring is needed. Biological methods are environmentally friendly, safe, least destructive, and cost-efficient. However, biological processes are often time consuming and only effective for low-to-moderate levels of heavy metals/metalloids. Combined remediation methods may overcome the limitations of single technology alone, but require complex operating conditions. As technology continues to evolve, it is generally agreed that the adopted method should not only have a remarkable effect on reducing the amount, bioavailability, and toxicity of the contaminants, but also cause minimal disturbance to the natural environment or local ecological systems. The ecological impact should be considered in the establishment of remediation goals and environmental criteria.

In addition, this review reveals the following key knowledge gaps and practical challenges, which should be addressed to advance the remediation technology:

- (1) The remediation criteria have shown a trend to shift from reducing the total concentration of the contaminants to lowering the fraction that is more leachable or bioavailable. Given the often inhibitive cost for removing total heavy metals from soil, treating the more risky fraction of the contaminants appears more practical. However, careful monitoring the residual metals in the soil is needed especially at sites that are subject to significant perturbation in biogeochemical conditions.
- (2) While the immobilization or stabilization approaches have been increasingly accepted in soil remediation practices, it is important to know whether immobilized metals are reversible and stable under natural and disturbed conditions. Long-term (years to decades) field experiments are needed to evaluate the stability and remobilization of the immobilized contaminants. While remediation companies are often held responsible for long-term stability of the immobilized

metals, a mechanism for long-term monitoring and liability for completed sites has been lacking. As a result, field data have been rare or lacking on the long-term effectiveness of the remediation practices.

- (3) It is highly desired to further investigate the molecular-level reaction mechanisms that govern the heavy metal/metalloid speciation and mobility. Such information may aid in development of mechanism-based models to predict longterm stability or mobility of metals under various environmental conditions. In addition, the information can provide sound scientific basis for improvement of current remediation techniques.
- (4) It has been a rule rather than exception that soil and groundwater are polluted with multiple pollutants including metals/metalloids and organic chemicals. There is a need to understand the impact of soil amendments on the stability of co-contaminants. Cautions should be exercised in the remediation process to minimize disturbance to the local biogeochemical conditions and to avoid mobilization of other co-contaminants. For example, addition of phosphate compounds to soil may mobilize arsenate.
- (5) The effects of soil amendments on soil properties and soil/ groundwater biogeochemical conditions should be measured at the field scale. Field studies should also determine bioavailability, phytotoxicity, and ecoreceptor endpoints to show reduction of risks. Conversely, the environmental fate of the amending agents in the soil should be followed under field conditions.
- (6) There is an urgent need for technologies suitable for remediating agricultural land contaminated with metals/metalloids, especially when active farming is practiced, as well as sites located in residential areas or soil in deep aquifers.
- (7) Further studies are needed to develop and test mechanistically sound models to predict the adsorption/reaction rates, desorption kinetics, and chemical speciation under field biogeochemical conditions. Such models are useful to gauge the effectiveness of the technology and to assess the longterm stability of immobilized heavy metals.
- (8) As remediation practices are increasingly constrained by complex factors that are beyond the conventional cost effectiveness, a systematic life cycle analysis method is needed to take into account technical, economic and sustainability issues in assessing field remediation technologies.

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