



## Review article

## Soil amendments for immobilization of potentially toxic elements in contaminated soils: A critical review



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## ABSTRACT

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Soil contamination by potentially toxic elements (PTEs) has led to adverse environmental impacts. In this review, we discussed remediation of PTEs contaminated soils through immobilization techniques using different soil amendments with respect to type of element, soil, and amendment, immobilization efficiency, underlying mechanisms, and field applicability. Soil amendments such as manure, compost, biochar, clay minerals, phosphate compounds, coal fly ash, and liming materials are widely used as immobilizing agents for PTEs. Among these soil amendments, biochar has attracted increased interest over the past few years because of its promising surface properties. Integrated application of appropriate amendments is also recommended to maximize their use efficiency. These amendments can reduce PTE bioavailability in soils through diverse mechanisms such as precipitation, complexation, redox reactions, ion exchange, and electrostatic interaction. However, soil properties such as soil pH, and clay, sesquioxides and organic matter content, and processes, such as sorption/desorption and redox processes, are the key factors governing the amendments' efficacy for PTEs immobilization in soils. Selecting proper immobilizing agents can yield cost-effective remediation techniques and fulfill green and sustainable remediation principles. Furthermore, long-term stability of immobilized PTE compounds and the environmental impacts and cost effectiveness of the amendments should be considered before application.

## 1. Introduction

Soil pollution is a type of land degradation that occurs when a range of natural or anthropogenic constituents exceed maximum permissible levels in natural soil environments (Hou and Ok, 2019; Liu et al., 2018). Potentially toxic elements (PTEs) from both natural and anthropogenic

sources can end up in the soil, and improper disposal of industrial and domestic waste, spills during industrial operation, overuse of agrochemicals, and mining and smelting operations are the most common activities leading to accelerated soil pollution. Soil contamination with potentially toxic elements (PTEs) (i.e., antimony (Sb), arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu),

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lead (Pb), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), selenium (Se), silver (Ag), tin (Sn), titanium (Ti), vanadium (V), and zinc (Zn) has been widely reported and has led to growing concerns regarding severe negative effects on living organisms, including humans (Li et al., 2015; Wang et al., 2018a). For example, PTE food chain contamination is a serious issue that threatens both animal and human health (Antoniadis et al., 2017b; Antoniadis et al., 2017d). A nationwide soil quality survey in China found that 16.1% of all soil samples exceeded recommended standards by China's Ministry of Environmental Protection, thereby undermining food quality and human health and drawing public attention to the severity of soil pollution in China (Hou & Li et al., 2017; Palansooriya et al., 2019c). More importantly, so-called cancer villages associated with soil pollution in China serve as notorious examples pinpointing the severe impacts of soil pollution on human health. A survey (Third National Survey on Causes of Death) identified 13 areas in China as cancer villages, with four (Yingdong District of Xinyang in Anhui Province, Shenqui and Jun counties in Henan Province, and Yingcheng in Hubei Province) exhibiting cancer death rates higher than the national average (Liu, 2010).

An estimated 12.6 million people have died worldwide in recent years from > 100 diseases caused by unhealthy environments such as contaminated soils (WHO, 2016). During the past decade, As poisoning and resulting adverse health effects have been reported in Bangladesh. Among that nation's population of 125 million, 35–77 million people have been affected by As poisoning, making it the largest known mass poisoning by contaminants in human history (Shakoor et al., 2019; Smith et al., 2000). Based on 2015 data, the Institute for Health Metrics and Evaluation and the World Health Organization (WHO) have reported 494,550 deaths and a loss of 9.3 million disability-adjusted life years resulting from long-term Pb exposure of humans (WHO, 2018). Young children are particularly susceptible to Pb poisoning due to ingestion of Pb-contaminated soil or dust, and many young children in Nigeria, Senegal, and many other countries have died from exposure to Pb-contaminated soil (Keller et al., 2017; WHO, 2018). Each year, > 600,000 children worldwide have mental retardation caused by elevated blood Pb levels (O'Connor et al., 2018a). With increasing risks to human health posed by contaminated soils, identifying and optimizing soil remediation techniques has become increasingly important.

Interest in soil remediation among the wider scientific community has been growing because of increasing land degradation and decreasing productive lands due to PTE contamination (Palansooriya et al., 2019a; Yoo et al., 2018). Many in situ and ex situ soil remediation techniques have been used to minimize risks associated with PTE contamination and to maximize arable land for agricultural production to ensure food security (Beiyuan et al., 2017b; Wang et al., 2015a). In situ technologies such as solidification/stabilization (Li et al., 2018b; Wang et al., 2018b; Wang et al., 2019c), immobilization (Wang et al., 2018c), soil washing/flushing (Beiyuan et al., 2018b), phytoremediation, and biological/microbial treatments, and ex situ techniques such as soil washing (Beiyuan et al., 2018a; Beiyuan et al., 2017c), vitrification land filling, and bioreactors are frequently used to minimize bioavailability of PTE contaminants (Kuppusamy et al., 2016; Wang et al., 2015b). These soil remediation techniques all have different overall working principles and specific advantages and disadvantages. Moreover, technique efficacy and cost effectiveness may significantly differ between laboratory tests and field practices (Khalid et al., 2017; Wang et al., 2018e). Among these methods, application of soil amendments to immobilize PTEs has been widely employed to remediate PTE-contaminated soils (Fig. 1), because of its fast and easy application and its commercial viability (Beiyuan et al., 2016; Wang et al., 2018d). Choosing appropriate immobilizing agents can deliver cost-effective remediation techniques and fulfill "green and sustainable remediation" principles because of their lower life cycle environmental footprints (Hou and Al-Tabbaa, 2014).

Increased interest in soil remediation research among the scientific

community brings an urgent need for advanced applications of soil amendments and integrated understanding of their function in soil. Research on low-cost and eco-friendly materials for the treatment of PTEs-contaminated soils has seen significant attention in the last years (Fig. 1); there is a great scientific interest on studying the impact of organic and inorganic soil amendments (e.g., biochar, compost, charcoal, and activated carbon, lime, fly ash, and red mud) on PTEs mobility in contaminated soils during the last twenty years. Recently, the total published papers reached > 3000 articles (Fig. 1, a, b). Therefore, it is worth to review these huge numbers of published papers on this topic and introduces a comprehensive dose of information to the relevant scientific community. Although, some peer-reviewed studies have focused on various soil amendments for PTE immobilization (e.g., Bolan et al. (2014); Kumpiene et al. (2008); Lwin et al. (2018); Mahar et al. (2015); Park et al. (2011)), however, a comprehensive comparison of all potential soil amendments and their applicability and efficacy to specific PTEs is needed for instructive evaluations of soil remediation's feasibility. Therefore, this review aims to be a comprehensive, authoritative, critical, and readable review of general interest to the chemistry community because it is unique enough to provide comprehensive information on the remediation of PTEs contaminated soils using low cost and environmental friendly soil amendments. The state-of-art about sources, characteristics, and potential environmental risks of PTEs as well as new approaches for immobilization of PTEs using different organic and inorganic amendments are presented and discussed in this review. Specifically, the scope of this review is to systematically evaluate the most recent studies related to soil amendments and PTE immobilization with respect to immobilization efficiency, underlying mechanisms, and field applicability. Moreover, we aim to highlight the further research needs of this field of study and direct attention toward novel research on soil amendments. We also discuss the behaviors and ecological risks of PTEs and status of immobilization in remediation techniques to highlight the necessity of acting promptly. The presented knowledge in this review is prerequisite for a better understanding of the sources and geochemical behavior of PTEs in soils to apply appropriate and efficient environmental soil amendments for PTEs immobilization. This article will appeal to a wide range of stakeholders including soil and water scientists, environmentalists, and researchers who are interested in improving the quality of environment. This review is expected to assist in making decisions in proper soil amendment selection for remediating PTE-contaminated soils to achieve the best and most sustainable remediation outcomes for different scenarios.

## 2. Potentially toxic elements (PTEs) in soils

### 2.1. Sources and occurrence

Potentially toxic elements can occur naturally in soils in varying concentrations depending on geochemical composition of source rocks and soil formation processes such as weathering sedimentation and volcanic eruptions (Cui et al., 2018; Li et al., 2017). Meanwhile, anthropogenic activities such as mining and smelting operations, oil and gas production, industrial production, military practices, and agricultural activities can also result in elevated soil PTE concentrations (Hou and Li, 2017; O'Connor et al., 2018c).

Soil PTE concentrations equal the sum of inputs from lithogenic and anthropogenic sources minus losses due to plant uptake, soil erosion, and leaching and volatilization of gaseous forms (Alloway, 2013) (Fig. 2). Lithogenic and anthropogenic PTE sources can be distinguished using isotope ratio analysis, enrichment factors of target and reference elements, geographic information system-based data, and multivariate statistical analysis (Davis et al., 2009; Yongming et al., 2006).

#### 2.1.1. Lithogenic sources

Lithogenic sources are soil parent materials from which PTEs are

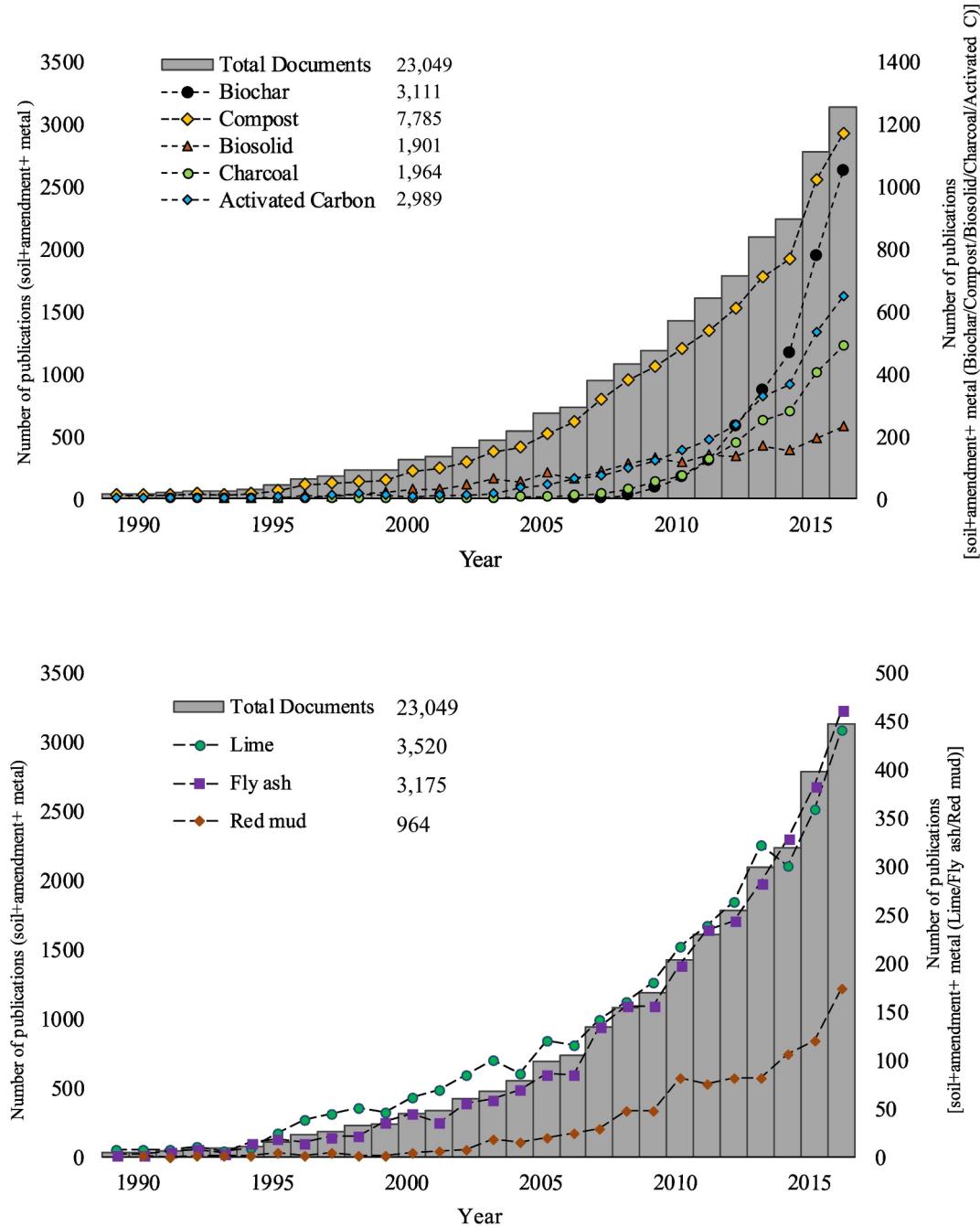
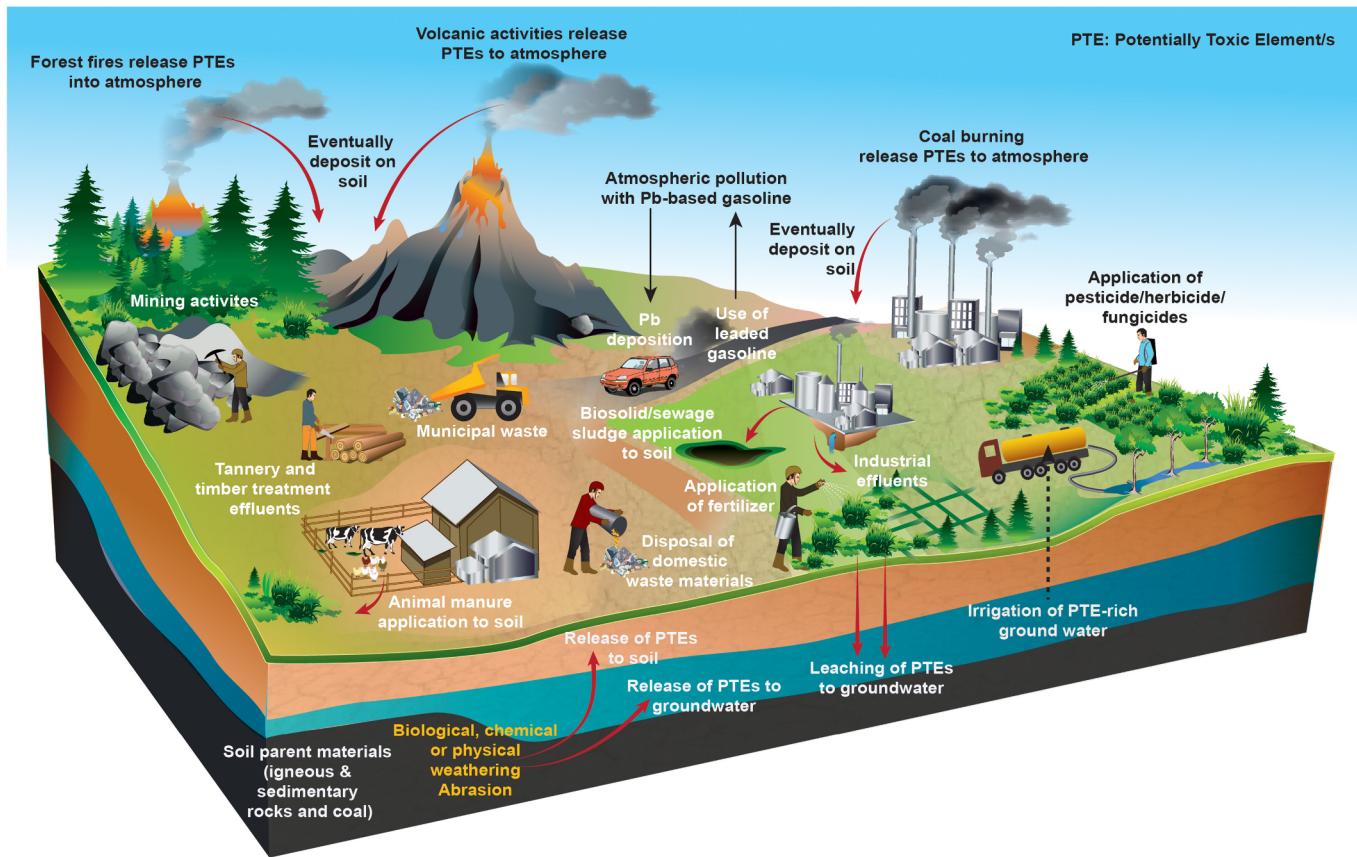


Fig. 1. Publications related to (a) organic and (b) inorganic soil amendments and potentially toxic elements from 1990 to 2017 (SCOPUS data base).

derived. Almost all PTEs can be found in soil formed through geological weathering, volcanic activities, or sedimentation (Cui et al., 2018; Li et al., 2017; Wong et al., 2006), (Fig. 2). During weathering, some constituent minerals of parent materials are released in soluble forms, with biochemical interactions between weathering products forming secondary minerals. Immobile PTEs and rare earth elements such as Zr, Hf, Th, Nb, and Sc are usually either concentrated in resistant phases or strongly adsorbed by secondary minerals, whereas mobile elements such as Ba, Sr, and Rb are derived mainly from leachable minerals such as feldspars, apatite, and micas (Alloway, 2013). A comparison of PTE concentrations from various soils around the world showed that Mn (418 mg/kg) and Ba (362 mg/kg) have the highest concentrations, which is consistent with their relative abundance in Earth's upper crust (Alloway, 2013). In volcanic areas, volcanic plumes and ashes are important PTE sources, with PTE abundance depending on secondary

mineral composition (Adamo et al., 2003; Navarro et al., 2008). People living near volcanic areas may have naturally higher PTE exposure than those in reference sites. For example, children living near Mt. Etna, Italy, show elevated intakes of As, Mn, U, and V (Varrica et al., 2014).

Lithogenic source rock types also significantly influence PTE abundance and distribution in soils. Black shales are known to have enriched organic matter content (usually 10%–20%) owing to oceanic anoxic events (Trabucho Alexandre et al., 2010) and contain significantly elevated PTE concentrations compared to the upper crust (Alloway, 2013; Zanin et al., 2010). Apatite ( $\text{Ca}_5(\text{F}, \text{Cl}, \text{OH})(\text{PO}_4)_3$ ) is a major phosphate mineral form that can serve as a raw material for P fertilizer manufacturing. Geochemical studies have shown that several PTEs are enriched in apatites through different mechanisms, such as formation of insoluble compounds with Pb and surface adsorption or complexation with Cu and Zn (Bolan et al., 2003g; Cao et al., 2004).



**Fig. 2.** Potentially toxic element (PTE) sources in soil ecosystems.

This raises the concern of leaching weakly bounded metals in minerals, which subsequently serves as an important source of PTE inputs to soils. Likewise, mineral ores result in higher soil PTE concentrations, whereas elevated concentrations in larger areas can be attributed to mining and smelting activities as anthropogenic sources.

Bedrock geological composition provides information on PTE background levels, which is helpful for identifying excessive PTEs from anthropogenic sources (Wong et al., 2006). However, this approach may have limitations in urban contexts where soils may have originated from more than one source and have been redistributed by human activities (Wong et al., 2006).

### 2.1.2. Anthropogenic sources

Ubiquitous anthropogenic sources also contribute to soil PTE concentrations. Among these sources, energy production, mining, metal smelting, waste incineration, and traffic emissions account for a significant portion of total PTE inputs to soils (Nicholson et al., 2003; Rinklebe and Shaheen, 2017; Shaheen et al., 2017d), (Fig. 2). Depending on the composition of coal used, coal combustion can release various PTEs into the atmosphere (Davis et al., 2009; Shaheen et al., 2014a). In China, most Hg found in urban soil is related to atmospheric deposition of fossil fuel combustion byproducts, especially from coal burning (Kuo et al., 2006; Wang et al., 2003). Moreover, India has been found to be the second largest atmospheric Pb emitter in Asia after China because of coal combustion (Das et al., 2018).

Elevated PTE concentrations can also be found near urban-rural transition zone locations where mining and smelting activities take place. Elevated PTE concentrations, predominantly of As, Cd, Hg, and Pb, have been found in soils near mining areas in Europe (Toth et al., 2016). Mine tailing dam failures have been reported in various places across the world (Hatje et al., 2017), which have resulted in contamination of downstream alluvial soil by metal(lloid)-containing

particles. Wastelands generated by mining activities in China amount to 1,500,000 ha, and this area has been increasing by 46,700 ha per year (Zhuang et al., 2009). Elevated soil As content usually found near Sb and Pb–Zn mining areas (Li et al., 2014). Additionally, smelting of Pb ores can put As particulates of up to 3 wt% into the atmosphere (Shin et al., 2018; Taylor et al., 2014). In this respect, some recent studies (Rinklebe and Shaheen, 2014; Shaheen et al., 2017d) found that high total PTE concentrations have accumulated in the floodplains of the Elbe and Wupper river systems in Germany. These high concentrations were most likely caused by contamination of Wupper River water and sediments by the discharge of waste from industrial activities such as textile bleaching, knife manufacturing, electroplating, and mining.

In urban soils, the sources of PTEs are usually complex, and include deposition of dust and aerosol particles, industrial activities, fertilizer and compost use in urban gardens, and the use of paints and other protective materials (Luo et al., 2012). GIS-based and multivariate statistical analyses have found that Cd, Cu, Pb, and Zn are commonly detected in urban soils contaminated by vehicle traffic, paint use, and other industrial discharges (Davis et al., 2009; Lee et al., 2006; Luo et al., 2012), whereas As and Hg primarily come from coal burning (Luo et al., 2012; Yang et al., 2011). Lead is the most distinctive urban soil PTE contaminant coming from paints and vehicle exhausts. In urban areas, dispersion and deposition of metal-containing particulate matter transports and redistributes PTEs. This process is influenced by multiple physical and environmental factors such as urban landscape, wind direction, and urban water runoff.

In agricultural areas, profiles of soil PTEs are more closely related to lithogenic sources; however, atmospheric transport and deposition of PTEs from fossil fuel combustion, industrial processes, waste incineration, and application of PTEs-containing products such as insecticides, herbicides, fungicides, algicides, and wood preservatives are also major sources (Alloway, 2013; Chen et al., 2008; Nicholson et al., 2003;

**Table 1**

Chemical behaviors of key potential toxic elements (PTEs) in soils.

TE	Chemical behaviors in soil	References
As	<ul style="list-style-type: none"> <li>-Oxidation states: +3, +5</li> <li>-Sorption: Mainly sorbed to Fe(oxy)hydroxides through inner-sphere bidentate and monodentate surface complexes.</li> <li>-Speciation: In natural waters, soils, and sediments, the As species of interest are arsenite oxyanions, As(V); arsenite oxyanions, As(III); monomethylarsonic acid, As(III); and dimethylarsinic acid, As(I). However, under natural environmental conditions, arsenic exists mainly in two species, arsenite (As (III)), which is mainly present under anaerobic conditions and arsenate (As(V)), which is mainly present under aerobic conditions.</li> <li>-Others: Shares chemical similarity with P; therefore, phosphates increase As mobility in soils.</li> </ul>	(Jia et al., 2013; LeMonte et al., 2017; Liu et al., 2002; Niazi et al., 2018b; Shaheen and Rinklebe, 2015b; Taylor et al., 2014)
Ba	<ul style="list-style-type: none"> <li>-Sorption and mobility: Not very mobile because it is easily precipitated as sulfates and carbonates and is strongly adsorbed by clays, oxides, and hydroxides; however, it is relatively mobile in acidic soils.</li> <li>-Bioavailability and plant uptake: Easily taken up by plants in acidic soils. Although Ba is reported to be commonly present in plants, it is not an essential plant tissue component. Ba mean contents in most plants range from 2 to 13 mg/kg.</li> </ul>	(Alloway, 2013; Kabata-Pendias, 2010)
Cd	<ul style="list-style-type: none"> <li>-Sorption: Forms inner-sphere complexes on surfaces, bound to organic matter (OM) at pH &lt; 6.5 and to Fe oxides at pH &gt; 6.5. Forms complexes with inorganic ligands or dissolved OM.</li> <li>Association with soil components: A great part of Cd is bound to humic acid. Cadmium carbonates might be found as a major Cd species in some soils, whereas a small amount of Cd sulfide might be found in other soils.</li> <li>-Mobility and bioavailability: Cd is highly mobile and thus is readily available for plant uptake. It has a long biological half-life in the human body (15–20 yrs).</li> <li>-Others: Forms precipitates in reduced soils containing S as CdS (solubility &lt; 0.1 µg/L).</li> </ul>	(Bi et al., 2006; Rinklebe and Shaheen, 2014; Shaheen et al., 2016)
Co	<ul style="list-style-type: none"> <li>-Oxidation states: Can exhibit +1 to +4 oxidation states, with +3 and +2 being the most common. Divalent Co(II) and trivalent Co(III) are the most important oxidation states of Co in aqueous solutions and depend on pH and redox potential (Eh) values.</li> <li>-Sorption: Tends to form labile outer-sphere complexes with various ligands as pH increases.</li> <li>-Others: Mobility increases under reducing conditions because it is closely associated with Mn due to chemical similarity.</li> </ul>	(Alloway, 2013; Shaheen et al., 2014b)
Cr	<ul style="list-style-type: none"> <li>-Oxidation states: +3, +6</li> <li>-Geochemical fractions: Residual and crystalline Fe oxide fractions are the Cr dominant fractions in most soils;</li> <li>Speciation: Can exist in several oxidation states ranging from the metallic form, Cr(0), to Cr(VI). The most stable oxidation states of Cr in the environment are Cr(III) and Cr(VI). The insoluble Cr(OH)<sub>3</sub> or Cr(III) is sorbed to soil colloids; Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> in strongly acidic soils. Cr(VI) is typically associated with oxygen as CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>.</li> <li>-Others: Cr(III) is less mobile and less toxic than Cr(VI) and is mainly found bound to OM.</li> </ul>	(Alloway, 2013; Antoniadis et al., 2017c; Rinklebe et al., 2016c; Shahid et al., 2017; Tchounwou et al., 2012)
Cu	<ul style="list-style-type: none"> <li>-Oxidation states: +1, +2</li> <li>-Sorption: Typically bound to inorganic and organic ligands.</li> <li>-Others: Effective cation exchange capacity is the best soil indicator for predicting Cu toxicity in most cases. Forms precipitates in reduced soil with sulfides.</li> </ul>	(Bi et al., 2006; Shaheen et al., 2017c; Tchounwou et al., 2012)
Hg	<ul style="list-style-type: none"> <li>-Oxidation states: 0, +2</li> <li>-Sorption: Strongly bound to OM and S;</li> <li>-Bioavailability: Roots serve as a barrier to Hg uptake (i.e., low availability from soil to plants).</li> <li>-Speciation: Determined by pH and Cl<sup>-</sup> concentrations in a soil solution. Mediated by microbial-assisted transformation. Forms soluble HgS<sub>n</sub><sup>2-</sup> anion in strongly alkaline soil.</li> </ul>	(Alloway, 2013; Beckers and Rinklebe, 2017; Tchounwou et al., 2012)
Ni	<ul style="list-style-type: none"> <li>-Oxidation states: Can occur in several oxidation states: +1 to +4, but only Ni (+1, +2, and +3) are stable over a wide range of pH and redox conditions found in soil environments;</li> <li>-Sorption: High affinity for soil OM.</li> <li>-Bioavailability: Quick uptake by plants as Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup></li> </ul>	(Alloway, 2013; Rinklebe and Shaheen, 2017; Tchounwou et al., 2012)
Mn	<ul style="list-style-type: none"> <li>-Oxidation states: +2, +4 (in soil)</li> <li>-Sorption: Tends to form labile outer-sphere complexes with various ligands as pH increases. Decreasing solubility with increasing pH.</li> <li>-Speciation: Water-soluble and exchangeable forms of Mn(II) and insoluble Mn oxides (mainly Mn (IV)).</li> <li>-Others: Mn(II)-oxidizing microbes can oxidize Mn(II) at all soil pH values, whereas reduction can be mediated by microbial metabolism.</li> </ul>	(Alloway, 2013; Tchounwou et al., 2012)
Mo	<ul style="list-style-type: none"> <li>-Oxidation states: +3 to +6</li> <li>-Sorption: Weakly bound to ligands such as Cl<sup>-</sup> and OH<sup>-</sup>. Adsorbed on Fe-hydroxide in acidic soils.</li> <li>-Bioavailability: Most mobile and bioavailable at pH &gt; 6.5 and least available under acidic conditions.</li> <li>-Speciation: Mo(IV) predominant under reducing conditions. Mo(VI) predominant under oxidizing conditions.</li> <li>-Others: Shares similar behaviors with P and S in soil. Becomes less available due to formation of Fe-Mo minerals.</li> </ul>	(Alloway, 2013; Shaheen et al., 2018; Shaheen et al., 2014c; Tchounwou et al., 2012)
Pb	<ul style="list-style-type: none"> <li>-Sorption: Strongly bound to humic matter (organic-rich soil) and to Fe oxides (mineral soil).</li> <li>-Speciation: PbS precipitates in reduced soils and forms Pb<sup>2+</sup> ions under oxidizing conditions.</li> <li>-Bioavailability: Soluble Pb-organic and Pb-hydroxy complexes. Roots serve as a barrier for plant uptake.</li> </ul>	(Bi et al., 2006; Okkenhaug et al., 2016; Rinklebe et al., 2016c)
Sb	<ul style="list-style-type: none"> <li>-Oxidation states: -3, 0, 3, 5 (mainly found as +3 and +5). Sb(+3) is predominant under low redox conditions (Eh &lt; 50 mV), whereas Sb(+5) is less stable in reducing environments. Sb (+5) might be a stable oxidation state even under reducing conditions.</li> <li>-Others: Sb(III) is more toxic than Sb(V) and is commonly found in ores of Ag, Cu, and Pb.</li> </ul>	(Herath et al., 2017b; Hockmann et al., 2014; Okkenhaug et al., 2013)

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**Table 1** (continued)

TE	Chemical behaviors in soil	References
Se	-Oxidation states: Present in nature primarily in oxidation states of +6 (selenite, $\text{SeO}_4^{2-}$ ), +4 (selenite, $\text{SeO}_3^{2-}$ ), 0 (elemental selenium, $\text{Se}^0$ ), and -2 (selenide, $\text{Se}^{2-}$ ). Se(+4) is the more toxic form. Selenium is subjected to transformation when redox conditions change, going from $\text{Se}(+6) \rightarrow \text{Se}(+4) \rightarrow \text{Se}(0) \rightarrow \text{Se}^{2-}$ , depending on Eh. Se (+4) and Se (+6) are predominant in soils with pH > 6. Negative oxidation numbers are affected by biological processes. -Sorption: Al- and Fe-oxides and hydroxides. -Competing anions: Sulfate, phosphate, and organic anions.	(Okkenhaug et al., 2016; Shaheen et al., 2014b)
V	-Oxidation states: +2 to +5. Under moderately reducing and oxidizing conditions, V(+4) and V(+5) species are dominant. Vanadium (+5) is the most mobile and toxic form and is thermodynamically stable in oxic environments, whereas vanadium (+3) might be expected to be predominant under euxinic (anoxic and sulfidic) conditions. -Geochemical fractions: Residual fraction of V is mainly dominant in most soils, followed by it bound to crystalline Fe oxides, to soil OM, to Mn oxides, and to low crystalline (amorphous) Fe oxides, and soluble + exchangeable. -Redox-induced mobilization: Mobilization in soils may be affected positively by soil pH, chemistry of (Fe)(hydr)oxides, and the release of aromatic organic compounds. -Sorption: Vanadium added to soils may be retained by clay, oxides, or OM. -Bioavailability: Tends to accumulate in plant roots.	(Alloway, 2013; Shaheen et al., 2019a; Shaheen and Rinklebe, 2018)

Shaheen et al., 2015b; Yang et al., 2018). Additional sources of PTE contamination include localized events such as flooding that carries PTEs and deposits them on flooded land downstream and corrosion of metals in building materials (Nicholson et al., 2003; Rinklebe et al., 2016a).

Multiple agricultural products are composed of metal- or metalloid-based compounds. These include As-based herbicides, Cd-, Cu-, Sn-, and Hg-based fungicides, As- and Hg-based pesticides, and Cu-, Cr-, and As-containing wood preservatives (Luo et al., 2007; Nicholson et al., 2003; Shaheen et al., 2015b; Yang et al., 2018). For example, inorganic fungicides applied apple orchards in Virginia, USA accounts for 156, 220, 263 and 1150 mg/kg of Cu, Zn, As and Pb levels, respectively (Alloway, 2013). Although some of these products have been banned because of their toxicity, existing contamination remains and could continue affecting soil for many decades (Alloway, 2013). Organic fertilizers such as poultry and livestock manures have also been widely supplied to soil (Huang et al., 2015; Nicholson et al., 2003; Shi et al., 2018). However, PTEs such as As, Cu, and Zn were originally added to animal feed as supplementary nutrients and growth promoters and thus lead to some organic fertilizers being a source of PTEs in soils (Bolan et al., 2004; Niu et al., 2013). In China, annual Zn input from livestock manures reached 96,000 t, accounting for approximately half of total Zn inputs to soil (Luo et al., 2009). In fact, livestock manures were the most significant inputs of Cu and Zn into soils in Europe and China (Nicholson et al., 2003). Inorganic fertilizers, such as those derived from phosphate rocks with Cd as an inherent component, may also induce PTEs to soil (Bolan et al., 2013c).

Industrial byproducts (e.g., flue gas dusts and various slags) that are reused on agricultural lands to reduce burden on landfills could also contribute to elevated soil PTE levels (Luo et al., 2009). Sewage sludges from wastewater treatment plants are considered beneficial for agricultural lands because of their high N, P, and organic matter contents. However, PTE concentrations in sewage sludges, which are sourced from human excreta, stormwater runoff, and industrial wastewater limit the amount that can be applied (Nicholson et al., 2003; Shaheen et al., 2017e).

Military activity and shooting sports can also introduce As, Cu, Mn, Mo, Ni, Pb, Sb, and Zn to soil due to oxidation and deterioration of spent ammunition (Alloway, 2013; Migliorini et al., 2004; Sanderson et al., 2015). At a shooting range, lead concentrations could reach as high as approximately 2000 µg/g (Murray et al., 1997), which stands in stark contrast to a baseline concentration of 70 µg/g or less (Migliorini et al., 2004). In Korea, 11,100 mg/kg of total Pb, approximately 16 times greater than the permitted 700 mg/kg value, was observed in soil at a military shooting range by the Korea Ministry of Environment (Ahmad et al., 2012b). In the same sites, Cu and Sb concentrations were

approximately 8 and 33 times higher than the acceptable limits of 150 mg/kg and 5 mg/kg, respectively (Ahmad et al., 2016b). In a clay pigeon shooting range in Japan, Pb concentrations reached 18,100 mg/kg in the surface soil (Hashimoto et al., 2009b). In addition to these PTEs, elevated concentrations of Zn have been found in shooting range soils (Okkenhaug et al., 2013).

In conclusion, PTEs can be reached to soil either from geogenic or anthropogenic sources; however, the potential mobility and associated risk of these elements differ widely based on their source (Shaheen et al., 2017d). The potential mobility of PTEs is the anthropogenically contaminated soils is much higher than the geologically contaminated soils. Although the naturally occurring PTEs are relatively immobile and rarely toxic; however, they may pose a potential risk to the environment, particularly under certain changes of soil pH and redox potential. Although soil pollution with anthropogenic PTEs and its remediation has been the focus of increasing research in the last few decades due to their toxic impacts on our ecosystems, soils that contain elevated levels of PTEs derived from geological sources have received scant attention, even though they provide some fascinating topics to study. Therefore, the geochemical behavior of PTEs and the associated risk and the amendments-induced mobility of these pollutants in soils varying in origin, characterization, and source of elements are worth to be reviewed.

## 2.2. Biogeochemical behaviors and environmental risks of PTEs in soils

Distribution of PTEs among geochemical fractions and species in soils is governed by multiple factors such as (i) mineral precipitation-dissolution, (ii) ion exchange and adsorption-desorption, (iii) complexation, (iv) pH and redox conditions, (v) biological (im) mobilization and transformation, and (vi) plant uptake and leaching (El-Naggar et al., 2019; El-Naggar et al., 2018). Table 1 summarizes chemical behaviors of key PTEs under various environmental conditions. Redox conditions strongly affect the geochemical behavior of PTEs that have multiple oxidation states such as As, Cr, Mn, Mo, Se, U, and V (Alloway, 2013; Middelburg et al., 1988; Rinklebe et al., 2016a; Rinklebe et al., 2016b; Rinklebe et al., 2016d; Shaheen et al., 2014b; Shaheen et al., 2014c). PTE mobility and speciation indicates ecosystem toxicity. Soil PTE fractions can be divided into various operationally defined fractions such as (i) an exchangeable fraction that is readily released to the environment due to changes in water and ionic composition, (ii) a carbonate-bound fraction susceptible to pH conditions, (iii) Fe- and Mg-oxide-bound fractions sensitive to pH and redox potential, (iv) an organic-bound fraction resulting from complexation and peptization with natural organic matter, and (v) a residual fraction consisting mainly of primary and secondary minerals (Bloom et al.,

2003; Frohne and Rinklebe, 2013; Rinklebe and Shaheen, 2014; Tessier et al., 1979). The first three extractable fractions (i.e., exchangeable, carbonate-bound, and oxide-bound) are considered to be potentially mobile fractions that strongly depend on pH and redox conditions to regulate PTE forms and solubility in soil (Shaheen and Rinklebe, 2014).

Microorganisms are the first to react to PTEs in soil, and microbial metabolisms can mediate PTE speciation change (Bolan et al., 2013b). For example, *Hg*-methylating bacteria can transform HgS stabilized by dissolved organic matter in soils into methylmercury (Graham et al., 2012). Additionally, microbes containing *arsM* genes, which are abundant in soil, are responsible for As methylation prior to plant uptake (Jia et al., 2013). Excess PTEs can also adversely influence the structure or function of microbial communities in soil (Schloter et al., 2003). Soil enzyme activities are related to PTE types and concentrations, and soil properties regulate the chemical behavior of PTEs in soil (Table 1) and thus PTE bioavailability. It has been reported that Cu and Pb tend to strongly bind to organic matter (Table 1), which explains why Pb toxicity on soil enzyme activities were offset by addition of soil organic matter (Bolan et al., 2003a; Xian et al., 2015).

Some PTEs, such as Cu, Mn, Zn, and Fe, are micronutrients for higher plants and deficiency of these micronutrients can impair proper plant function and hinder plant yield; however, excessive amounts can reduce soil productivity by reducing or altering microbial communities and causing toxicity to plants (Alloway, 2013; Yang et al., 2018). Thus, ecological risks are assessed in terms of bioavailable or phytoavailable values. Elevated soil PTE concentrations may also lead to phytotoxic effects on plants by producing increased amounts of reactive oxygen species in response to metal stresses (Alloway, 2013; Tchounwou et al., 2012). Manure-borne metals tend to accumulate and thus raise potential phytotoxicity risks (Tchounwou et al., 2012). Phytoavailability of PTEs may greatly depend on plant type, element type, and soil properties (Antoniadis et al., 2017d; Salam et al., 2019). Based on a critical review of PTE phytoavailability, Menzies et al. (2007) concluded that total Cd, Cu, Ni, Pb, and Zn concentrations had no correlation with their phytoavailable fractions, because only free PTE ions in soil solutions are phytoavailable than mineral-phase or strongly complexed PTEs in soils.

Accumulated and elevated PTE concentrations in crops have raised increasing public health concerns (Antoniadis et al., 2017a; Bolan et al., 2013c; Chen et al., 2018; Liu et al., 2017; Zang et al., 2017). In addition, accumulated and elevated PTE concentrations account for a large and varying portion of PTE outputs (i.e., losses by leaching, surface runoff, crop harvest, and gaseous emission) depending on element type, vegetation, soil, and local climate (He et al., 2005). Elevated PTE amounts (e.g., Pb concentrations of 0.80–1.5 mg/kg and Cd levels of 0.05–0.76 mg/kg) were detected in corn grain near a smelting area (Bi et al., 2006). Insoluble PTE forms may be transformed into more bioavailable forms through biochemical interactions in the rhizosphere of plant roots, thereby increasing PTE uptake. For instance, Bolan et al. (2013a) observed P-induced As mobilization resulting in competition between phosphate ions and As ions. Mechanisms and pathways of plant root PTE sequestration also have crucial effects on translocation of PTEs to different parts of the plant. For example, Pb and Hg are mainly found accumulated in roots, which serve as a barrier to plant uptake (Table 1). Concentrations of PTEs in corn plant root tissue were found to positively correlate with those in soil samples (Bi et al., 2006). Cultivation of rice in paddy soil is highly susceptible to As accumulation because the flooded conditions used to grow rice favor As mobility (Rahman et al., 2018; Xu et al., 2008). A study of sites near zinc smelting areas in Guizhou, China, found that the majority of Pb remained within the top 20 cm of the soil due to low mobility (Table 1), whereas Zn can migrate to at least 50 cm, indicating that Zn has a stronger mobility than Pb (Bi et al., 2006). Mobility of Cd was found to be the highest in soil, where total concentrations were up to 10 mg/kg even deeper than 1 m (Bi et al., 2006; Li et al., 2013). Additionally, a study of urban soils in China revealed that PTE mobility decreased in the order of Cd, Zn, Pb, Cu, Ni, and Cr (Luo et al., 2012).

Regarding human health, the major exposure pathways to PTEs from soil are food consumption, soil ingestion, dermal absorption, and inhalation (Antoniadis et al., 2017a; Antoniadis et al., 2017d; Li et al., 2014; Niu et al., 2013). Interior paint, playground soil and dust, household and common area dust, and ceramic cookware are main sources of elevated blood Pb concentrations among children (Etchevers et al., 2015; Peng et al., 2019). Cobalt, Cr, Cu, Mn, Mo, Se, Sn, V, Zn, and Fe are micronutrients for animals and humans and act as constituents or activators of enzymes (Alloway, 2013); however, over-exposure can cause adverse health effects. Arsenic, Hg, and Pb are all well-known environmental neurotoxins and Ba, Be, Cr, Cu, Mn, and Ni are known as occupational toxins (Davis et al., 2009).

Moreover, PTEs in soils can transfer to other environmental compartments, such as aquatic ecosystems, through erosion and surface runoff from agricultural land (Cui et al., 2005; Luo et al., 2007). These contribute to the outputs of PTEs from soil. Leaching of PTEs is usually more prominent in sandy and acidic soils than in fine soils because of the lack of strong binding between PTEs and soil colloids in the former. Although Pb migration in soil is slow, some studies have shown potential risks for contaminating growing plants and groundwater resources (Antoniadis et al., 2017b; Antoniadis et al., 2017d; Lee and Kim, 2010; Qin et al., 2018). Losses of PTEs caused by surface runoff are usually associated with the transport of particulates containing metal-organic complexes (He et al., 2005).

We can summarize that PTEs in soil can enter other environmental compartments or be bio-accumulated by plants, further entering the food chain and raising serious concerns over potential adverse risks to human health and ecological systems. The toxicity of PTEs depends on an element's speciation and corresponding bioavailability, which are governed by environmental conditions such as redox potential, soil minerals, and soil microorganism communities. Therefore, it is important to understand soil PTE behaviors and bioavailability to estimate relevant environmental risks and adopt appropriate remediation methods.

### 3. Immobilization of PTEs in soils

Because soil contamination by PTEs is a considerable environmental concern, immobilizing or reducing the mobility and bioavailability of PTEs in soil ecosystems are crucial. Immobilizing PTEs refers to stabilizing them or reducing their mobility in soil with the aim of reducing plant and human bioavailability and reducing leaching of PTEs to groundwater (Bolan et al., 2014; Park et al., 2011).

#### 3.1. Soil properties and processes affecting PTE immobilization in soil

Mobilization and immobilization of soil PTEs mainly depends on PTE chemical forms or binding ability, which are governed by soil properties and environmental processes. Soil geochemical processes such as sorption and desorption; precipitation; interactions with C, Fe, Mn, Al, S, and organic matter; and redox processes (especially in wetlands and water-logged farmlands) play a significant role in PTE mobility (Shaheen et al., 2014b; Shaheen et al., 2016). Soil properties such as soil pH, ion exchange capacity, electrical conductivity (EC), redox potential (Eh), organic matter (OM) content, soil clay mineral and metal oxide type and concentration, bulk density, particle-size distribution, and texture control PTE mobilization or immobilization in soils for all these phenomena (Beiyuan et al., 2017a; Sparks, 2003).

In general, when soil pH increases, cationic PTEs tend to decrease their mobility and solubility, whereas the mobility and solubility pattern for anionic PTEs is the opposite. The concentration of  $H^+$  and  $Al^{3+}$  ions is higher in acidic soils, thus competition between  $H^+$  and  $Al^{3+}$  ions and PTE cations for adsorption sites results in decreased PTE adsorption. Decreased pH also leads to a decreased negative charge in variable charge soils, thereby decreasing adsorption of cationic PTEs (Sparks, 2003). In addition, acid-induced dissolution of oxides and their

sorption sites can trigger decreased adsorption when pH is low (Essington, 2015). In contrast, element hydrolysis at high soil pH levels leads to formation of metal hydroxo complexes, resulting in strong and preferential adsorption of PTEs (Bradl, 2004). Three possible explanations have been identified for increased Cd<sup>2+</sup> adsorption with increasing pH: i) high pH causes an increase in surface negative charge, thereby increasing Cd<sup>2+</sup> adsorption (in variable-charge soils); ii) high pH results in the formation of metal cation hydroxy species (e.g., CdOH<sup>+</sup>) that are favorably adsorbed over metal cations; and iii) precipitation of Cd<sup>2+</sup> as Cd(OH)<sub>2</sub> (Bolan et al., 2014; Bolan et al., 1999; Sparks, 2003). For oxyanions such as As, solubility might increase as pH increases, which can be mainly ascribed to desorption of anionic PTEs with a reduction of positive charges on soil surfaces with increasing pH (Bradl, 2004). However, at any fixed pH value, PTE adsorption capacity could be decreased by an increase in initial PTE concentration, apparently due to the gradual saturation of adsorption sites (Naidu et al., 1994). Redox potential significantly and directly affects PTE mobility in soils, especially for PTEs such as Cr, Se, and As, which have mobility and toxicity highly dependent on the soil's redox environment. For example, under reduced Eh soil environments, Cr (VI) can be converted to Cr (III), making it less bioavailable and thus less toxic to organisms (Bradl, 2004). In contrast, decreased Eh can allow As(V) to be transformed into As(III), which is more toxic and mobile (Bissen and Frimmel, 2003). In addition, under reduced Eh conditions, Fe and Mn oxides/hydroxides tend to dissolve, as a result, As on Fe and Mn oxides is released to the environment (Bourg and Loch, 1995). Using X-ray absorption spectroscopy (XAS), Hashimoto and Kanke (2018) illustrated changes in the oxidation state of As (As(V), As(III)) and As<sub>2</sub>S<sub>3</sub>-like species relative to the soil redox gradient during a series of flooding-drying periods. Redox insensitive PTEs may not change their oxidation status with respect to mobility; however, reductive dissolution of Fe and Mn oxides and hydroxides can greatly affect release and mobility by desorbing the sorbed PTEs (Bourg and Loch, 1995; Rieuwerts et al., 1998). Soil EC is another chemical property that determines PTE mobility in soils. Increased soil EC is usually associated with an increase in macro- and micronutrients such as Ca, K, Mg, and Na in soils, which can compete with cationic PTEs for adsorption sites (Du Laing et al., 2008; Naidu et al., 1994). Consequently, this may lead to increased PTE mobility in saline soil, which has higher EC. In particular, Cd and similar PTEs tend to form complexes with chlorides in saline soil, increasing their mobility (Hu et al., 2016). However, under highly reduced conditions (-100 mV), the availability of sulfide-rich soil facilitates the precipitation of Cd with sulfide minerals, which is always the immobilized form regardless of soil salinity (Du Laing et al., 2008; Kashem and Singh, 2001). Sulfide's importance with respect to Cd immobilization was also noted in reduced paddy soils where Cd solubility decreased rapidly with enhanced CdS formation (Furuya et al., 2016; Hashimoto and Yamaguchi, 2013; Ok et al., 2011). Because cation exchange capacity (CEC) determines soil ion binding capacity, CEC is also considered as an important factor affecting PTE mobility in soil. Soils with higher CEC generally cause increased cationic PTE binding capacity, leading to reduced PTE mobility in soil (Cao et al., 2003; Kelebemang et al., 2017). Depending on soil type, CEC and PTE mobility can be affected to various degrees. In particular, the presence of clay minerals, metal oxides, and OM in soils increase CEC and provide a greater surface area for PTE sorption (Finzgar et al., 2007). Consequently, in soils with higher quantities of these compounds, PTE mobility tends to be low. Soil organic matter consists of decomposing plant and animal residue and soil fauna and microbiota, and is characterized by the presence of humus or humic substances as well as non-humic substances. The availability of these constituents thus reduces PTE mobility in soils (Bradl, 2004). Ion exchange, complexation, and adsorption are major mechanisms involved in PTE retention by OM. Functional groups such as phenols, carboxyl, carboxylate, and amino groups in OM can act as binding sites for PTEs (Park et al., 2011; Quenea et al., 2009). Moreover, with increased pH, these functional

groups tend to increase and form organo-metal complexes that are more stable at higher pH levels (Zeng et al., 2011).

Metal oxides such as Al, Fe, and Mn oxides and oxyhydroxides are important components for immobilization of PTEs in soils. Strong specific adsorption, special affinity for metal oxides, and formation and precipitation of specific minerals—for instance, Pb–Mn minerals such as coronadite—may account for reducing PTEs mobility in soils (Zeng et al., 2017). Redox potential is a crucial factor that determines metal oxide concentration in soils. Under reduced conditions, oxide concentrations (especially for Fe and Mn oxides) are often low, whereas the opposite occurs under oxidized conditions. Thus, PTE immobilization by metal oxides is more effective under oxidized conditions (Rinklebe et al., 2016d). Clay minerals such as chlorite, kaolinite, illite, smectite, zeolite, bentonite, and vermiculite can act as sinks for PTE through mechanisms such as ion exchange and specific adsorption (Barton, 2002; Rieuwerts, 2007). Isomorphous substitution leads some phyllosilicate minerals, such as smectite and vermiculite, to have permanent negative charges on their surfaces, whereas some clay minerals have charges that are variable or pH-dependent (Barton, 2002; Bolan et al., 1999). Soils high in clay minerals exhibit higher adsorption capacities owing to permanent or variable charges, thus facilitating greater PTE retention. Soil origin also affect the metals mobility in soils; for example, the Alfisol, Oxisol, and Ultisols of Brazilian soils have varying PTE adsorption capacities among the soil types, which was attributed to different levels of OM, clay minerals, and Fe oxide contents in the studied soils (Gomes et al., 2001).

We conclude that mobilization of PTEs in soils mainly depends on soil origin and properties (e.g., particle size distribution, clay minerals, soil pH, ion exchange capacity, redox potential, and the content of organic matter, sesquioxides, carbonate and sulfur) because these properties affect the sorption capacity of the soil and also affect the metals distribution among their geochemical fractions and thus control the potential mobility of the metals in soils. Depending on these physicochemical properties, metals mobility may largely vary among different soil types.

For example, the mobility of PTEs in soils and the potential associated risk depend on their geochemical behavior, which highly be affected by soil properties and metal type. For example, the changes of soil E<sub>H</sub> during the flooding / drying conditions and the E<sub>H</sub>-dependent changes of pH may regulate other processes such as oxides dissolution, organic matter decomposition, and sulfide formation, which indirectly influence speciation and solubility of PTEs. Therefore, understanding the specific soil properties and processes affecting PTE mobility is necessary before developing suitable remediation techniques or selecting proper soil amendments.

### 3.2. (Im)mobilization as a green and sustainable remediation approach

Depending on PTE type, soil physicochemical properties, and availability of resources such as soil amendments, soil remediation can be achieved through both mobilization and immobilization techniques. Before selecting mobilization or immobilization remediation techniques, it is necessary to understand the 1) nature of specific PTEs, 2) exposure pathways and adverse effects, and 3) interactions between soil amendments and PTEs. Mobilization techniques deal with phytoremediation or phytoextraction, in which released PTEs can be taken up by higher plants that are subsequently recycled or discarded (Shaheen et al., 2019e; Wang et al., 2019a). In contrast, immobilization techniques aim to prevent PTE mobility by various soil amendments (Fig. 3), and minimize PTE bioavailability to plants, animals, and humans, and reduce leaching capability to groundwater. Ex situ or in situ immobilization is often carried out by incorporating suitable soil amendments into contaminated soils. Various soil amendments have been investigated for PTE immobilization (Fig. 1). Promising outcomes were observed using organic amendments, such as biochar, and inorganic amendments, such as phosphates, clay minerals, metal oxides,

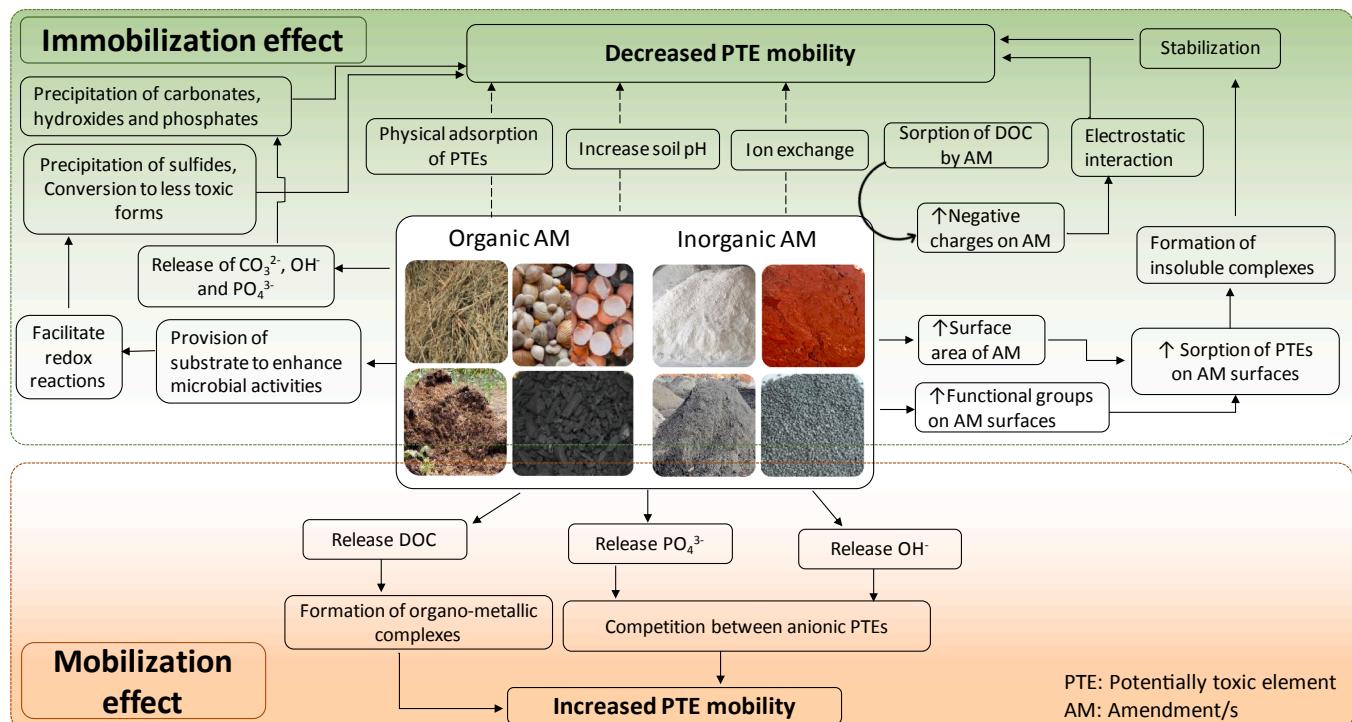


Fig. 3. Mechanisms of PTE immobilization and mobilization from various organic and inorganic soil amendments.

and liming materials. In addition to serving as a PTE immobilization agent, soil amendments could also improve plant growth and soil health by providing nutrients, increasing water holding capacity, and improving soil structure. The application of low-cost soil amendments to immobilize PTEs is a promising way to achieve environmentally sound and cost-effective remediation.

Ex situ immobilization techniques are often carried out by excavating soils from their place of origin and treating them off-site. This method could be fast and easy to control, and could also be designed as a closed system with lower ongoing operation and monitoring costs. However, ex situ remediation techniques have some limitations, such as the high costs involved in soil excavation and transport, greater soil ecosystem disturbance, and higher health risks for workers handling and transporting contaminated soil. In situ immobilization is considered more convenient than ex situ remediation. Although it takes more time to decontaminate the soil, in situ remediation is less expensive, causes less soil ecosystem disturbance, and is easier to adopt than ex-situ techniques. Use of soil amendments to immobilize PTEs in soil can be considered as in situ remediation technique. However, immobilizing PTEs by adding soil amendments is not always possible in some cases. For example, some soil amendments may have contradictory effects on the PTEs mobilization and phytoavailability as presented in Fig. 3 and Table S1 and reported by many studies (e.g., Shaheen and Rinklebe (2015a), Shaheen et al. (2017e) and Rinklebe and Shaheen (2015)).

From the above-mentioned reviewed studies, we can summarize that selecting a proper amendment is a crucial aspect of efficient immobilization process. Otherwise, depending on contaminant types, soil amendments that mobilize a metal can be utilized for enhancing its phytoextraction, which may make the phytoremediation process shorter.

#### 4. Soil amendments for immobilization of PTEs

Application of soil amendments has proven effective at immobilizing PTEs in soils based on physicochemical changes that occurred in the soil after application. This section will provide

information on soil amendments and their potentials for use in immobilizing PTEs in contaminated soils.

##### 4.1. Organic amendments

Organic soil amendments are known to improve soil structure and increase soil OM content, thereby enhancing soil's ability to hold nutrients and moisture. This in turn contributes to improved plant growth and health. In addition, certain organic soil amendments, such as biochar, compost, and animal wastes, have been recognized as PTE immobilizing agents because of their abilities to restrain PTEs through different mechanisms (Ahmad et al., 2017; Park et al., 2011; Shaheen et al., 2017e). Table 2 summarizes the effects of different organic soil amendments on PTE immobilization and their underlying mechanisms.

###### 4.1.1. Processed animal wastes

Animal wastes from the dairy, beef cattle, swine, and poultry industries (e.g., cow dung, pig manure, and chicken manures/litter) are commonly available and used by farmers as fertilizers because of their high nutrient content. Although application of animal-originated waste is primarily aimed at improving soil fertility, some of these amendments have been found to be suitable for reducing PTE mobility in soil (Bolan et al., 2003a; Bolan et al., 2003e).

Applying cow manure and bone meal to contaminated soil has resulted in significantly reduced leaching and phytoavailability of Cd and Zn in soil (Houben et al., 2012). Leaching of Cd was reduced by 63.1% with cow manure and by 72.9% with bone meal. Similarly, cow manure and bone meal reduced Zn soil concentrations by 89.0% and 89.1%, respectively. In addition, researchers observed reduced Cd, Zn, and Pb levels in white lupin shoots compared to a control treatment (Houben et al., 2012). Application of bone meal has also been found to reduce Cu, Fe, Mn, Ni, and Zn in contaminated soil (Shaheen et al., 2017e). This could be explained by several mechanisms. One is that the high alkalinity and high carbonate content of these amendments adsorb and retain PTEs in an unexchangeable form. Additionally, high OM content, especially in cow manure, can bind PTEs via chemisorption and reduce their mobility (Shaheen et al., 2017e; Zhao et al., 2014). One study

**Table 2**  
Effects of organic soil amendments on immobilization of potentially toxic elements (PTEs) in soils.

Amendment type	Amendment	TE	Soil condition	Experiment Type	QA/QC measures	Dose, % control	Effectiveness (compared to control)	Mechanisms/reasons for immobilization	Reference
Animal wastes	Egg shell	Cd	Mine-contaminated soil	Incubation and pot experiments	3 replicates ANOVA test	5	16.11% immobilization	Increased soil pH; formation of Cd-carbonate, phosphate, or hydroxide	(Lim et al., 2013)
	Chicken bone			Leaching pot experiment	5 replicates ANOVA test	3.33	11.69% immobilization 72.9% reduction in leaching; 60.1% reduction in phytoavailability 63.1% reduction in leaching; 86.5% reduction in phytoavailability	Increased soil pH; formation of Cd-carbonate, phosphate, or hydroxide Alkalinity, ion exchange, and chemisorption	(Houben et al., 2012)
	Cow manure	Cd, Zn, and Pb-contaminated soil							
Bone meal									
Bone meal	Fe	Sewage effluent-irrigated soils	Pot experiments	3 replicates Certified reference materials for each element ANOVA test	1	53.6% decrease in mobility 25.8% decrease in mobility 24.6% decrease in mobility 23.7% decrease in mobility	Increase of soil pH and formation of metal carbonate	Increase of soil pH and formation of metal carbonate	(Shaheen et al., 2017e)
Egg shell	Mn								
Bone meal	Mn								
Bone meal	Ni								
Mussel shell powder	Pb	Shooting range soil	Incubation experiment	3 replicates ANOVA test	5	92.5% decrease in bioavailability; 48.5% decrease in bioavailability	Increase of soil pH facilitated precipitation of Pb-hydroxide and Pb-phosphate	Increase of soil pH facilitated precipitation of Pb-hydroxide and Pb-phosphate	(Ahmad et al., 2012b)
Cow bone powder	Pb	Shooting range soil	Incubation experiment	3 replicates ANOVA test	5	84.8% decrease in bioavailability; 34.5% decrease in bioavailability	Increase of soil pH facilitated precipitation of Pb-hydroxide and Pb-phosphate	Increase of soil pH facilitated precipitation of Pb-hydroxide and Pb-phosphate	(Ahmad et al., 2012b)
Oyster shell	Pb	Shooting range soil	Leaching experiments	3 replicates ANOVA test	2.5	38.6% reduction in water soluble Pb 22.7% reduction in water soluble Pb 45% reduction in water soluble Pb	Increase of soil pH led to precipitation of Pb as $\text{OH}_2\text{PbCO}_3$ , and $\text{Pb}(\text{CO}_3)_2(\text{OH})_2$ . Ion exchange with Ca and Mg in lime-based waste materials	Increase of soil pH led to precipitation of Pb as $\text{OH}_2\text{PbCO}_3$ , and $\text{Pb}(\text{CO}_3)_2(\text{OH})_2$ . Ion exchange with Ca and Mg in lime-based waste materials	(Ahmad et al., 2012c)
Mussel shell									
Egg shell	Pb	Mine-contaminated soil	Incubation experiment	3 replicates ANOVA test	5	31.09% immobilization	Ion exchange with Pb; precipitation of pyromorphite-type products	Ion exchange with Pb; precipitation of pyromorphite-type products	(Lim et al., 2013)
Chicken bone									
Mussel shell	Sb	Army firing range soil	Incubation and pot experiments	3 replicates ANOVA test	5	59.5% immobilization ~13.9% decrease in phytoavailability	Increased soil pH; formation of phosphate Increased exchangable Sb due to increased soil pH; competitive effect with phosphate and increased phytoavailability	Increased soil pH; formation of phosphate Increased exchangable Sb due to increased soil pH; competitive effect with phosphate and increased phytoavailability	(Ahmad et al., 2014)
Cow manure	Zn	Cd, Zn, and Pb-contaminated soil	Leaching pot experiments	5 replicates ANOVA test	3.33	89% reduction in leaching; 64.3% reduction in phytoavailability	Reduced leaching; increased alkalinity; reduced phytoavailability; strongly reduced concentration of free ion metal species	Reduced leaching; increased alkalinity; reduced phytoavailability; strongly reduced concentration of free ion metal species	(Houben et al., 2012)
Bone meal	Zn	Sewage effluent-irrigated soils	Pot experiments	3 replicates Certified reference materials for each element ANOVA test	1	89.1% reduction in leaching; 88.9% reduction in phytoavailability 32.9% decrease in mobility	High content of carbonates and formation of Zn carbonate fraction	High content of carbonates and formation of Zn carbonate fraction	(Shaheen et al., 2017e)
Egg shell									
Bone meal									
Poultry manure	Pb	Shooting range soils	Incubation experiment	NA	1–10	Decreased Pb solubility	Formation of chloropyromorphite.	Formation was inhibited in part by the presence of dissolved organic carbon in the soil.	(Hashimoto et al., 2009a; Hashimoto et al., 2009b)
Manure, collected from a local farm	Cd	Heavy metal contaminated soil	Filed experiment	RCBD	~3.3	38–41% reduction in $\text{NH}_4\text{NO}_3$ -extractable Cd 77–83% reduction in $\text{NH}_4\text{NO}_3$ -extractable Pb 43–47% reduction in $\text{NH}_4\text{NO}_3$ -extractable Zn	Formation of stable complexes with organic compounds	Formation of stable complexes with organic compounds	(Vrinceanu et al., 2019)
Pb									
Zn									

(continued on next page)

Table 2 (*continued*)

Amendment type	Amendment	TE	Soil condition	Experiment Type	QA/QC measures	Dose, %	Effectiveness (compared to control)	Mechanisms/reasons for immobilization	Reference
Biochar (BC)	Dead pig-derived BC	Cd	Soil spiked with dibutyl phthalate, Cd, and Pb (low organic C)	Laboratory leaching study	3 replicates ANOVA test	1	38% reduction in leaching loss	BC's higher specific surface area, surface alkalinity, pH, and mineral contents	(Qin et al., 2018)
Rice straw BC	Cd	Municipal effluents irrigated soil	Pot experiment	3 replicates RCBD ANOVA test	5	~35, 47, and 57% decrease in roots, shoots, and grains	Increase of soil pH and Si contents in plant tissues and in soil solution	(Abbas et al., 2017)	
Hardwood-derived BC	Cd	Multi-element-contaminated soil	Pot experiment	3 replicates RCBD ANOVA test	50	~98% decrease in soil pore water Cd concentration	Increase of pH reduced solubility of metals	(Beesley et al., 2010)	
Soybean stover BC	Cu	Shooting range soil	Incubation experiment	3 replicates RCBD ANOVA test	2.5	16.2% reduction in bioavailability; 29.1% reduction in leaching	Precipitation; adsorption by electrostatic interactions and $\pi$ - $\tau$ electron donor acceptor	(Vithanage et al., 2017)	
Rice straw BC	Ni		Incubation and pot experiment	3 replicates ANOVA test	5	~51, 42, and 65% decrease in roots, shoots, and grains	Increase of soil pH and Si contents in plant tissues and soil solution	(Ahmad et al., 2014)	
Oak wood BC	Pb	Army firing range soil	Incubation experiment	3 replicates ANOVA test	5	55.50% decrease in phytoavailability; 84% decrease in exchangeable Pb	Increased soil pH facilitated sorption of Pb onto kaolinite	(Ahmad et al., 2014)	
Vegetable waste BC/500	Pb	Contaminated rice paddy soil	Incubation experiment	3 replicates ANOVA test	5	95.1% of significant reductions in the exchangeable fraction	Electrostatic interaction and Pb precipitations on BC surface; complexation with O-containing functional groups	(Igalavithana et al., 2017a)	
Wood bark	Pb	Contaminated upland followed field soil	Incubation experiment	3 replicates ANOVA test	5	98.9% of significant reductions in the exchangeable fraction	Alkalinity and high phosphorous content of BCs attributed to Pb immobilization	(Igalavithana et al., 2017b)	
Dead pig-derived BC	Pb	Contaminated lowland paddy soil	Incubation experiment	3 replicates ANOVA test	5	77.7% decrease of exchangeable fraction	Alkalinity and high phosphorous content of BCs lead to Pb immobilization	(Igalavithana et al., 2017b)	
Soybean stover BC	Pb	Contaminated upland soil	Incubation experiment	3 replicates ANOVA test	1	91.5% decrease of exchangeable fraction	BC's higher specific surface area, surface alkalinity, pH, and mineral contents	(Qin et al., 2018)	
Oak wood BC	Sb	Soil spiked with dibutyl phthalate, Cd, and Pb (low organic C)	Laboratory leaching study	3 replicates ANOVA test	1	71% reduction in leaching loss	Precipitation; adsorption by electrostatic interactions and $\pi$ - $\tau$ electron donor acceptor	(Vithanage et al., 2017)	
Hardwood-derived BC	Zn	Multi-element-contaminated soil	Incubation experiment	3 replicates RCBD ANOVA test	2.5	7.7% reduction in bioavailability, 19.2% reduction in leaching	Sorption of Sb onto Fe (hydro)oxide of BC by the formation of inner-sphere complexes	(Ahmad et al., 2014)	
Hickory nut shell BC	Cd	Paddy field near a mining area	Pot experiment	3 replicates RCBD ANOVA test	5	53.44% decrease in phytoavailability	Increased pH reduced solubility of metals	(Beesley et al., 2010)	
Maize straw BC			Field experiment	3 replicates RCBD ANOVA test	50	~76% decrease in soil pore water Zn concentration	Abundant pore structure and binding sites	(Zhang et al., 2019)	
Wheat straw	Cd	Paddy filed	Field experiment	3 replicates RCBD ANOVA test	1.1	42.4% reduction in DTPA-Cd	Precipitation of metals with $\text{CO}_3^{2-}$ and/or $\text{PO}_4^{3-}$	(Cui et al., 2016b)	
Pb			Pot experiment	3 replicates RCBD Mean comparison by LSD test	2.2	53.6% reduction in DTPA-Cd	Binding of Cd and Pb to the inner biochar particles	(Garrido et al., 2012)	
Biosolids	Sewage sludge	Cu	Cu mine tailing site	Pot experiment	10	1.1	34.4% reduction in DTPA-Cd	Increased soil pH	(Jamal Khan and Jones, 2008)
Sewage sludge	Cu	Soil contaminated by mine tailings: Caquenes area	Batch sorption experiment	2 replicates ANOVA test	4.7	50.4% reduction in DTPA-Cd	63% increase in sorption onto biosolids	(Garrido et al., 2012)	
		Soil contaminated by mine tailings: Requinoa area				14.2–50.3% reduction in exchangeable Pb	Availability of high amounts of organic matter (OM) in sewage sludge provided new sites for sorption of Cu		
						43% reduction in plant-available metals	30% reduction in Zn leaching	(Antoniadis, 2008)	

*(continued on next page)*

**Table 2 (continued)**

Amendment type	Amendment	TE	Soil condition	Experiment Type	QA/QC measures	Dose, % control	Mechanisms/reasons for immobilization	Reference
Biosolid	Zn-spilled agricultural soil		Leaching experiment	2 replicates				
	Cu	Contaminated agricultural soil: fluvial and calcareous soils	Batch sorption experiment	3 replicates			Biosolid-born OM increased sorption sites Formation of inner-sphere complexes that increased Cu sorption	(Shaheen et al., 2017a)
Compost	Green waste compost	Cd	Multi-element-contaminated soil	Pot experiment	ANNOVA test	2.5	~28% reduction in Cu sorption into soil ~43% reduction in Cu sorption into soil	
	Green waste compost	Cd	Contaminated soil from dismantled Zn smelter	Batch leaching experiments	3 replicates	50	82% decrease in soil pore water Cd concentration	(Beesley et al., 2010)
Agricultural postharvest waste compost		Cd	Agricultural soil spiked with Cd and Ni	Pot experiment	ANNOVA test	20	47% reduction in leaching	
				RCBD	3 replicates	1.25	Formation of complexes between metals and OM Increased soil pH; increased soil OM content	(van Herwijnen et al., 2007)
Plant residues	Green waste compost	Zn	Multi-element-contaminated soil	Pot experiment	ANNOVA test	50	11%-13% reduction in availability of Cd in dry soil	(Shaheen et al., 2017b)
	Green waste compost	Zn	Contaminated soil from dismantled Zn smelter	Batch leaching experiments	3 replicates	20	18.8% reduction in available Cd and 69.5% reduction in Cd concentration in shoots of maize	
Rice straw		Cd	Cd- and Pb-spiked soil	Pot experiments	ANNOVA test	1	8.8% reduction in available Cd and 66.9% reduction in Cd concentration in shoots of maize	
				ANNOVA test			Rice and wheat straws are rich in cellulose, hemi-cellulose, lignin, and silica which provide binding sites for metals	(Xu et al., 2016)
Wheat straw	Rice straw	Pb	Hg-contaminated paddy soil	Incubation experiment	3 replicates	0.5-9.0	13.5% reduction in available Pb bioavailability of inorganic Hg	(Zhu et al., 2015)
	Rice straw/root	Hg	Cd- and Pb-spiked soil	Pot experiments	ANNOVA test	1	27.8% reduction in available Pb	
	Wheat straw	Pb		ANNOVA test			Large amounts of cellulose, hemicellulose, lignin, and silica provide binding sites for metals	(Xu et al., 2016)

NA: Not available; RCBD: Randomized Complete Blocks Design.

employing the XAS technique (Hashimoto et al., 2009a) used poultry waste to immobilize Pb in shooting range soil and found that Pb was immobilized in part because  $\text{PbCO}_3$  was transformed to  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ . Animal derived wastes such as eggshell, mussel shells, oyster shells, and chicken bones are commonly available as food wastes with high liming characteristics due to their high carbonate, phosphate, and hydroxide contents. Increased soil pH due to high liming characteristics facilitates PTE immobilization in soil (Ahmad et al., 2012a; Ahmad et al., 2014).

Ahmad et al. (2012b) reported that the application of 5% (w/w) mussel shell and cow bone to shooting range soil reduced Pb bioavailability by 92.5% and 84.8%, respectively. Similarly, Lim et al. (2013) also observed a 59.5% immobilization of Pb in soil amended with 5% (w/w) chicken bone. Immobilization of Pb can be attributed to precipitation of Pb-hydroxide, Pb-carbonate, and Pb-phosphate in the soil (Ahmad et al., 2012c; Almaroai et al., 2014). In contrast, Houben et al. (2012) observed increased Pb leaching in a leaching column experiment using cow manure and bone meal. This is because high levels of dissolved organic carbon (DOC) in the soil enhanced the organometallic complexes (complexation of Pb by organic ligand), thereby increasing Pb mobility in the soil (Hashimoto et al., 2009c; Park et al., 2011). Li et al. (2016) evaluated the intensive chicken manure compost application on Cd mobilization and phytoavailability by a field investigation. When the manure applied at lower rates ( $< 54 \text{ t ha}^{-1}$ ), decreased Cd phytoavailability was resulted, whereas higher rates ( $> 108 \text{ t ha}^{-1}$ ) increased the Cd phytoavailability due to the formation of soluble metal-DOC complexes in soil.

The above results show that the various animal wastes can be used as PTE immobilization in contaminated soils, yet care should be taken when applying strong DOC releasing agents, as well as selecting appropriate dosages to avoid increasing PTE solubility in soils. In addition, application of iron oxides such goethite or biochar together with animal manure is recommended as iron oxides and biochar have preferential sorption ability for DOM (Li et al., 2018a; Ohno et al., 2007). Thus, it may reduce the formation of soluble PTE-DOM complexes and thereby minimizing the PTE mobility in soil. On the other hand, combined application of goethite/biochar and animal manure will bring added advantages for crop production in PTE contaminated soils. Because nutrient rich amendments can act as sources of nutrients for plant growth while stabilizing DOM and immobilizing PTEs in soils. Introduction of secondary pollutants such as some PTEs, antibiotics and pathogens is another issue associated with animal manure-soil application. Hence, we suggest two strategies to overcome the issue; i) composting could increase the biodegradation of contaminants during thermophilic phase and ii) conversion of manure in to biochar by pyrolyzing at higher temperatures ( $> 700^\circ\text{C}$ ) can break down organic and microbial contaminants while immobilizing unnecessary elements in manure. In this way animal manure can efficiently be used in contaminated soils while utilizing as a nutrient source for plant growth.

#### 4.1.2. Biochar

The past few years have seen an increasing interest in applying biochar to immobilize PTE in soils (Fig. 1a). Biochar can immobilize PTEs in contaminated soils while improving soil quality and can significantly reduce crop uptake of PTEs (O'Connor et al., 2018c; Palansooriya et al., 2019b). However, increased PTE mobilization in soil can also result after biochar application depending on the type of biochar, soil conditions, and PTE species (Igalavithana et al., 2017b; Shaheen et al., 2019c). Therefore, selecting a type of biochar suitable for remediating soils contaminated with multiple PTEs requires careful examination.

Ahmad et al. (2017) evaluated the significance of variable biochar properties and soil types on PTE mobility in contaminated soils using a batch leaching experiment. They observed a significant reduction in Pb and Cu leaching in alkaline soil ( $> 93\%$ ) using biochar produced at  $300^\circ\text{C}$  through precipitation of metal phosphates and surface complexation mechanisms. In acidic soils, they observed a 100% reduction

in Pb and Zn mobility with biochar produced at  $700^\circ\text{C}$ . In contrast, biochar increased Sb and As mobility in both soil types because of competition with phosphate and repulsive electrostatic forces between Sb and As anions and biochar surfaces. Likewise, Gu et al. (2018) observed increased As and Sb mobility in metal mine tailings using biochar derived from *Arundo donax* L. produced at  $600^\circ\text{C}$ . Igalavithana et al. (2017b) reported an 84.6% increase in exchangeable As in contaminated soil from wood bark biochar, resulting from increased pH and competition between  $\text{OH}^-$  and  $\text{HAsO}_4^{2-}$  ions. Moreover, application of chicken manure biochar increased reduction of As(V) to As(III), resulting in increased As mobility in the amended soils (Choppala et al., 2016). Conversely, some studies have suggested that increased soil pH and electrostatic interaction between biochar surfaces and PTEs were the main mechanisms responsible for immobilizing Cd, Cu, and Zn in biochar-amended soils (Beesley et al., 2010; Vithanage et al., 2017). Furthermore, increased soil pH caused by applying bamboo and rice straw biochars was capable of reducing Cd, Cu, Pb, and Zn mobility in contaminated paddy soil (Lu et al., 2017).

Organic C content is one of the most important factors determining PTE mobility in soil (Chen et al., 2019; Kunhikrishnan et al., 2017). High DOC in soil facilitates the formation of soluble metal complexes, thus increasing metal mobility (Shaheen et al., 2019c). Biochar produced at high temperatures has a relatively stable and insoluble carbon pool with lower DOC concentration, which reduces metal mobility (Awad et al., 2018; Zhao et al., 2018). For example, applying holm oak biochar pyrolyzed at  $650^\circ\text{C}$  showed a 66% and 77% reduction in pore water Cd and Zn concentrations, respectively (Egene et al., 2018). Immobilizing these two PTEs was mainly attributed to increased pH and decreased DOC contents in the amended soil. In particular, PTE immobilization can be attributed to sorption of DOC by biochar and a subsequent increase of negatively charged functional groups on biochar surfaces that can adsorb Cd and Zn from the soil (Egene et al., 2018).

Effective immobilization of Pb has been demonstrated with the application of various biochar types through several possible mechanisms (Moon et al., 2013; Shen et al., 2018a). For instance, Ahmad et al. (2012b) reported a 75.8% reduction in Pb bioavailability with oak wood biochar pyrolyzed at  $400^\circ\text{C}$ . Soybean stover biochar produced at  $700^\circ\text{C}$  achieved an 88.1% reduction in exchangeable Pb in soil at a military shooting range (Ahmad et al., 2016b). Moreover, a 95% reduction in Pb mobility has been observed using the same biochar type in contaminated agricultural soil (Ahmad et al., 2016a). Reduction of Pb in biochar-treated soils was mainly achieved because of the precipitation of Pb as chloropyromorphite ( $\text{Pb}_5[\text{PO}_4]_3\text{Cl}$ ) and hydroxylpyromorphite ( $\text{Pb}_5[\text{PO}_4]_3\text{OH}$ ). In addition, Cr mobility, bioavailability, and phytotoxicity have been successfully reduced by applying biochar to soil contaminated by tannery waste (Herath et al., 2017a). This suggests that Cr retention in biochar can be explained by mechanisms such as adsorption via  $\pi-\pi$  electron donor-acceptor interactions and pore diffusion (Shaheen et al., 2019d; Xia et al., 2019). A new trend in biochar-based immobilization is modifying biochar with other materials, to yield superior properties (Igalavithana et al., 2019; Iris et al., 2019; Yang et al., 2019). Compared to unmodified corncob biochar, MgO-coated corncob biochar reduced soil Pb leaching by 50.71% as revealed by toxicity characteristic leaching procedure (TCLP) (Shen et al., 2018b). Increased surface area, precipitation of  $\text{Pb}(\text{OH})_2$  and  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ , and cation- $\pi$  interaction have been identified as Pb immobilization mechanisms. In another study, rice husk biochar modified with non-toxic elemental S reduced Hg concentrations in TCLP leachates by approximately 99% (O'Connor et al., 2018b). This reduction was attributed to the formation of solid phase  $\text{HgS}$  due to the strong binding affinity S toward Hg. Additionally, biochar application showed considerable reduction in PTE mobility in reduced contaminated soils. Although both the biochar amended and unamended soils behaved similarly, decreased dissolved PTE concentrations indicated that biochar is an effective amendment for immobilizing PTE even under dynamic redox conditions (Rinklebe et al., 2016b).

Assessing the effectiveness of biochar in field scale is important. A review conducted by O'Connor et al. (2018c) evaluated 29 field studies on application of biochar for PTE immobilization in contaminated lands in 8 different countries. The study revealed that numerous factors involve in PTE immobilization in biochar amended soils such as biochar properties, feedstock type and application rate, biochar mixing depth, crop type, soil properties and meteorological factors. Moreover, the increased crop yield in biochar amended soils showed the potential of biochar as a fertilizer for plant growth, and thereby can reduce the use of mineral fertilizer. However, it should be noted that the ageing effect of biochar (for instance leaching of alkalinity) over the time may reduce the efficiency in PTE immobilization (O'Connor et al., 2018c).

#### 4.1.3. Biosolids/sewage sludge

Although the terms biosolid and sewage sludge are used interchangeably, there are subtle differences between them. Biosolids are nutrient-rich organic materials derived from sewage sludge treated in the wastewater treatment process. Properly treated and processed biosolids are used as fertilizers and soil amendments for improving and maintaining productive soils and enhancing plant growth (USEPA, 2018). Biosolids are also known as an effective sink for reducing PTE bioavailability in contaminated soils. However, because biosolids are a municipal byproduct, they are a range of contaminants. Therefore, application of exceptional quality biosolids is recommended as they contain reduced pathogens and odor (lower vector attraction) and lower concentrations of specific metals (Bolan et al., 2003a; Bolan et al., 2003b; Park et al., 2011).

Shaheen et al. (2017a) indicated that biosolids could be used to immobilize Cd, Cu, Pb, and Zn in soils with higher metal content; however, care should be taken when applying biosolids to soils with a lower pollution level as this can increase metal desorption and consequently increase environmental risks. A leaching column experiment conducted on Cd-contaminated soils (80 and 200 mg kg<sup>-1</sup>) showed that composted biosolids can immobilize Cd more than composted pine bark and spent mushroom compost (Tapia et al., 2010). The lowest leaching percentage was observed for biosolids (0.2%), whereas composted pine bark and spent mushroom compost showed relatively higher Cd leaching (4.0% and 0.7%, respectively). The study concluded that greater humification of OM and higher inorganic component contents, such as Fe, in the biosolids facilitated Cd immobilization (Tapia et al., 2010). In addition, Fe and Mn oxides in biosolids have been found to play a significant role in immobilizing PTEs because of the irreversible adsorption of PTEs into metal oxides (Mamindy-Pajany et al., 2014). Biosolid may also contain some plant nutrients and could be useful in crop production in contaminated soils. A field study conducted by Placek et al. (2016) found that the application of biosolid increased the soil pH, CEC, and of humic acids content, enabling Cd, Zn, and Pb immobilization, while facilitating plant growth by providing plant nutrients such as N and P. In this regard, integrated remediation approaches such as application of biosolid together with phytoremediation is suggested to maximize resource use efficiency in remediating PTE contaminated soils.

Biosolid-derived dissolved organic matter (DOM) content and soil properties should be considered before applying biosolids to soil. Formation of dissolved organo-metallic complexes with biosolid-derived DOM led to decreased sorption of Ni, Cu, and Pb in biosolid-amended soil compared to unamended soil (Liu et al., 2007). Soil characteristics such as text could determine the effectiveness of biosolids at PTE immobilization. Sewage sludge-amended contaminated sandy and clay soils showed increased Cu adsorption compared to control soils, resulting from increased sorption sites following soil amendment (Garrido et al., 2012). However, the amended sandy soil showed lower Cu adsorption than the amended clay soil, indicating that clay content was a determining factor in Cu adsorption magnitude (Garrido et al., 2012). In contrast, application of sewage sludge into soils with low OM content and low clay content increased soil organic

carbon concentration, enhancing Zn retention and reducing Zn leachability (Antoniadis, 2008). Furthermore, Tripathy et al. (2006) examined Cd, Cu, Ni, Pb, and Zn adsorption and distribution in three soil types (i.e., acidic alfisol, neutral red alfisol, and alkaline black vertisol) amended with sewage sludge. Although applying sewage sludge altered soil properties and PTE adsorption capacities to a certain extent, they found no effect on PTE distribution patterns in the amended soils. The study revealed that biosolid application effectiveness mainly depends on soil properties and the type and concentration of PTEs in the soil (Tripathy et al., 2006).

These results may suggest that more appropriate estimates for biosolid application should be obtained from site-specific information when selecting biosolids to amend contaminated soil. Because biosolids contain some impurities (Feizi et al., 2019; Shaheen et al., 2019b), biosolid quality must be conspired along with soil properties before applying. However, here we suggest that the conversion of biosolid to biochar would be a promising way to increase the use efficiency of biosolid. During the pyrolysis process, microbial and organic contaminants in biosolid are subjected to thermal breakdown, and PTEs such as As and Hg tend to volatilize during the thermal conversion process (Paz-Ferreiro et al., 2018; Van Wesenbeeck et al., 2014). Thus, the risk of applying original biosolid could be reduced up to a certain extent while utilizing waste materials in efficient way.

#### 4.1.4. Compost/plant residues

Composting is a process of humifying and stabilizing organic waste, in which microbial and enzyme activities accelerate organic waste degradation, converting it into humic substances, mineral ions, CO<sub>2</sub>, and H<sub>2</sub>O through mesophilic, thermophilic, and maturation phases (Bialobrzewski et al., 2015; Lu et al., 2014). The resulting compounds in the compost (i.e., humic substances, mineral ions, and microorganisms) can enhance PTE immobilization in agricultural soils, thereby reducing ecological and environmental risks associated with PTEs (de la Fuente et al., 2011; Udovic and McBride, 2012). Huang et al. (2016) reported that applying compost can minimize risks of crop failure and economic losses and reduce human health risks from PTEs. Plant-derived composted organic amendments/green compost have commonly been used to immobilize PTEs in contaminated soils.

Udovic and McBride (2012) tested the effects of household/garden compost, consisting of food scraps and biodegradable plastic and paper, discarded greenhouse soil mix containing peat moss, and wood-based animal bedding, on Pb and As bioavailability in contaminated apple orchard soils. Adding 10% (w/w) compost led to a significant reduction in potential Pb bioavailability (up to 12.3-fold reduction), whereas it increased As bioavailability (up to 3.1-fold increase). This could be attributed to increased soil pH, phosphate compound contents, and humic materials along with the compost addition. Lead tends to be less soluble at higher pH levels. In addition, the formation of strong complexes of Pb and humic materials and Pb-phosphate (Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) precipitation are possible Pb immobilization mechanisms in the studied soils. As shown by Milojković et al. (2016), compost derived from *Myriophyllum spicatum* can immobilize Pb, Cu, Cd, Ni, and Zn through the presence of hydroxyl, carboxyl, carbonyl, and phenyl functional groups is the compost that act as main binding sites for PTEs. In contrast, As is more soluble and mobile at higher soil pH levels because chemisorption is not favorable for anions such as AsO<sub>4</sub><sup>3-</sup> and AsO<sub>3</sub><sup>3-</sup> when pH is higher (Newton et al., 2006; Niazi et al., 2018a). Similarly, Mehmood et al. (2017) reported that applying commercial compost may hinder As sorption sites in clay loam soil. The higher CEC and clay content of clay loam soil contributed to greater negative charges in soil colloids. Thus, repulsion between negatively charged groups in compost and As oxyanions for sorption of soil colloids (i.e., anion exclusion) increased As mobilization in the soil (Mehmood et al., 2017). A soil's relative dryness is an important factor in determining the effectiveness of compost in soil remediation. Compost derived from agricultural postharvest wastes showed decreased Cd solubility and mobilization in

dry soil, but not in wet soil. In contrast, Ni showed decreased solubility and mobilization in both dry and wet soils. In this respect, applying plant-derived compost along with biochar may be an effective solution for increasing compost's immobilization efficiency. Karer et al. (2015) showed that applying garden green waste compost together with poplar woodchip biochar exhibited the best results for reducing Cd and Zn concentrations in soil while increasing ryegrass growth. These results clearly indicate that PTE and soil chemical properties as well as soil type need to be carefully considered when applying compost for the purpose of immobilizing PTEs.

Returning crop residues to the soil rather than burning them is strongly encouraged in many countries to minimize air pollution and for sustainable agriculture. In this regard, many studies have investigated the effects of plant residues on soil quality, particularly regarding PTE immobilization. Incorporation of dried or composted rice straw into the soil in upland or lowland farming is a common practice. Shu et al. (2016) assessed the mobilization of Hg in soils treated with different rice straw types (i.e., dry straw, composted straw, straw biochar, and straw ash). They found that composted straw treatments decreased methyl-Hg phytoavailability, indicating a methyl-Hg immobilization effect. This was attributed to the strong binding of methyl-Hg with particulate OM in amended rice straw. Conversely, dry straw treatments led to elevated methyl-Hg levels due to high levels of DOM developed by rice straw during decomposition. Zhang et al. (2018) made a similar observation, that incorporating rice straw resulted in a 28%–136% increase in methyl-Hg levels in Hg-contaminated paddy soil. Furthermore, Zhu et al. (2015) observed increased methyl-Hg and decreased inorganic-Hg levels in Hg-contaminated soil after applying raw rice residues such as rice roots and straw. Greater mobilization of methyl-Hg in soils amended with rice residues were mainly attributed to enhanced microbial activity and/or higher DOM production, which may promote formation of Hg-S-DOM complexes upon rice residue application (Shu et al., 2016; Zhu et al., 2015).

We conclude that compost and plant residues have varying effects on PTE immobilization depending on material maturity levels and composition as well as soil properties. Moreover, it is recommended to apply plant residues to soil after composting rather than direct incorporation, to minimize the PTE mobilization effect caused by increased DOM or microbial activities.

#### 4.2. Inorganic amendments

Many efforts have been made to immobilize PTEs in contaminated soils using different inorganic soil amendments, which can be either synthetic or mined materials (Table 3). Clay minerals, lime, gypsum, phosphates, coal fly ash, and metal oxides are inorganic amendments commonly used in soil remediation. Table 3 summarizes PTE immobilization effectiveness and underlying immobilization mechanisms of different inorganic amendments.

##### 4.2.1. Clay minerals

Clay minerals are naturally occurring minerals found in Earth's surface, most of which are identified as hydrated aluminosilicates (Rautureau et al., 2017). Three clay mineral types have been identified: (1) 1:1 clay minerals such as serpentine and kaolinite, (2) 2:1 clay minerals such as montmorillonite and vermiculite, and (3) 2:1:1 or 2:2 clay minerals such as chlorites (Bergaya and Lagaly, 2006; Sparks, 2003). In addition to these silicate clay minerals, Si, Al, and Fe oxides, hydroxides, and hydroxy-oxides also occur as small quantities of hematite, goethite, and gibbsite in the soil clay fraction (Barton, 2002). Because of their physicochemical properties, clay minerals show superior PTE immobilization performance in contaminated soils (Shaheen and Rinklebe, 2015a). In addition, clay minerals are relatively abundant and low cost, including different bentonite compounds, zeolite, sepiolite, and palygorskite, making them good natural scavengers of PTE in soil and biosolid treated soils (Feizi et al., 2019).

The addition of Ca-bentonite and Na-bentonite reduced the mobility of various PTEs in contaminated soils (Houben et al., 2012; Sun et al., 2015). For example, adding Na-bentonite and Ca-bentonite reduced the labile fraction of Zn by 24% and 31%, Cd by 37% and 36%, Cu by 41% and 43%, Ni by 54% and 61%, and Pb by 48% and 41% compared to a control, respectively (Usman et al., 2006). Usman et al. (2006) reported that applied clay minerals improved wheat shoot dry matter production by decreasing shoot PTE concentration below phytotoxicity levels. Moreover, Shaheen et al. (2015a) observed that applying bentonite leads to a significant reduction of water-soluble Ni (58.7%) and Zn (83%) in contaminated floodplain soil. Similarly, Shaheen and Rinklebe (2015a) reported that Cd and Pb can successfully be immobilized in contaminated floodplain soils using bentonite. Reduction in PTE mobility in bentonite-amended soil can be attributed to bentonite's larger surface area and stronger sorptive capacity (Kumararaja et al., 2016). Increased pH after applying bentonite is another mechanism that reduces PTE mobility (Lahori et al., 2019). Increased soil pH lowers metal ion solubility by forming precipitates and increases bentonite's PTE adsorption through a reduced inhibitory effect of  $H^+$  (Kumararaja et al., 2014). Zeolite has also been used as an immobilizing agent in many studies. Putwattana et al. (2015) observed a 17% reduction in Zn availability after applying 5% zeolite to contaminated soil. Li et al. (2009) reported that applying natural zeolite to Pb-polluted garden soil reduced Pb concentration in the edible parts of rapeseed by 30% due to reduced Pb bioavailability. Other studies have also recommended zeolite as a potential soil amendment for immobilizing PTEs because of the soil pH increases following zeolite addition (Tahervand and Jalali, 2017; Tica et al., 2011). In contrast, applying zeolite increased the soluble and exchangeable fraction of Cd and Pb in floodplain soil by 5.5% and 6.3% compared to a control, respectively (Shaheen and Rinklebe, 2015a).

Sorption effect has been identified as a plausible mechanism for PTE immobilization in clay mineral-amended soils (Rinklebe and Shaheen, 2015; Usman et al., 2006). These studies found that PTEs can be sorbed into clay minerals through different mechanisms due to the variable and permanent charges on their surfaces. In addition, outer-sphere complexation, inner-sphere complexation, lattice diffusion, and isomorphic substitution within the mineral lattice are possible PTE immobilization mechanisms (Yi et al., 2017). However, it has also been stated that most clay minerals have net negative charges, which enable adsorption of more cations (Barton, 2002). Thus, applying clay minerals with greater negative charges would be appropriate to immobilize cationic PTEs in soil. For instance, Sun et al. (2015) found that applying bentonite reduced Cd and Pb mobilization caused by outer-sphere complexation (ion exchange) of Cd and inner-sphere binding of Pb to bentonite's mineral edges. Houben et al. (2012) documented that leaching of Cd, Zn, and Pd in contaminated soils could be decreased using bentonite through chemisorption and ion exchange mechanisms. Moreover, Liang et al. (2014) reported that surface complexation of Cd sepiolite and palygorskite functional groups was the predominant mechanism involved in immobilizing Cd in metal-polluted paddy soil.

Alkaline clay minerals such as bentonite, sepiolite, and palygorskite would have better PTE immobilizing effects by increasing soil pH after application (Lahori et al., 2019; Yi et al., 2017). When soil pH is high, precipitation was found to be the predominant process in the presence of anions such as  $CO_3^{2-}$ ,  $OH^-$ ,  $SO_4^{2-}$ , and  $HPO_4^{2-}$  (Park et al., 2011). An in situ immobilization field experiment carried out on severely polluted paddy soil revealed that sepiolite and palygorskite immobilized Cd by increasing soil pH, and consequently forming  $CdCO_3$  and  $Cd(OH)_2$  precipitates (Liang et al., 2014). Similarly, Houben et al. (2012) reported that leaching of Cd, Zn, and Pd could be decreased by bentonite's liming effect.

These studies confirm that clay minerals are more likely to have net negative charges, thus it is recommended to use them for cationic PTE immobilization in contaminated soil. Moreover, the above discussion advances our knowledge on clay minerals' role in PTE immobilization

**Table 3**  
Effects of inorganic soil amendments on immobilization of potentially toxic elements (PTEs) in soils.

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Table 3 (*continued*)

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**Table 3 (continued)**

Amendment type	Amendment	TE	Soil condition	Experiment type	QA/QC measures	Dose, %	Effectiveness (compared to control)	Mechanisms/reasons for immobilization	Reference
Commercially available lime	Cd-contaminated paddy field	Filed experiment	3 replicates			12.9–18.2% reduction in available Cd			
Dolomite	Zn	Heavy metal contaminated soil	Filed experiment	Randomly arranged plots Soil sampling; composite of randomly collected 5 samples from the plots ANOVA test RCB	~3.7	52.2–69.5% reduction in DTPA-extractable Zn	Increase in soil pH Formation of oxides and carbonate precipitates	(Vrinceanu et al., 2019)	
Metal oxides	Goethite	Cd	Contaminated paddy soil	Field experiment	0.03–0.1	67.3 to 76.5% reduction in CaCl <sub>2</sub> extractable Cd	Liming effect of the amendment	(Bian et al., 2016)	
	Cd	Sewage-sludge-treated soil	Pot experiment	3 replicates ANOVA test	1	16% reduction in labile fraction	NA	(Usman et al., 2006)	
Hematite	Ni	Zn				22% reduction in labile fraction			
Iron grit	Pb	Cd, Zn, and Pb-contaminated soil	Leaching pot experiments	5 replicates ANOVA test	3.3	14% reduction in labile fraction	Reduced leaching due to increased pH and formation of Fe oxide on which metals can quickly sorb	(Houben et al., 2012)	
Zn						83% reduction in leaching	Reduced leaching due to increased pH and formation of Fe oxide on which metals can quickly sorb		
Red mud	Cd	Farmland around a Pb and Zn smelter	Field experiment	3 replicates	5	92.9% reduction in leaching; 24.3% reduction in phytoavailability	Reduced leaching due to increased pH and formation of Fe oxide on which metals can quickly sorb	(Wang et al., 2018)	
	Pb					67.95% reduction in DTPA-extractable Cd	Increase in soil pH		
Cu						64.21% reduction in DTPA-extractable Pb	High iron content in red mud can adsorb and combine with heavy metal		
Zn						43.73% reduction in DTPA-extractable Cu			
						63.73% reduction in DTPA-extractable Zn			
Phosphates	Triple superphosphate	Al	Sewage effluent-irrigated Cr soil	Pot experiments	1	55.2% decrease in availability	NA		
	Phosphate rock	Ni		Certified reference materials for each element		81.1% decrease in availability	Reduction of Cr <sup>6+</sup> to Cr <sup>3+</sup> by reduced sulfur species and Fe <sup>2+</sup> ; formation of insoluble salts	(Shaheen et al., 2017e)	
	Mono-ammonium phosphate	Zn	Municipal and sewage effluents irrigated soil	Field experiment		21.9% decrease in mobility	Formation complexes with Ni		
	Diammonium phosphate	Cu	Cu-mine tailing site	Pot experiment	0.8	33.3% decrease in mobility	Formation of Zn-phosphate complexes	(Qayyum et al., 2017)	
	Fe			RCBD		~56% reduction in bioavailable Cd	Cd fixation in the form of Cd phosphates, Cd carbonates, and various stable Cd complexes; Cd precipitation and surface adsorption on the amendment		
Novaphos	Pb	Sewage-sludge-treated soil	Pot experiment	3 replicates ANOVA test	2.3	21% reduction in plant-available metals	Formation of insoluble complexes	(Jamal Khan and Jones, 2008)	
Synthesized apatite	Pb	Shooting range soil	Pot experiment	4 replicates Mean comparison by LSD test	0.05	21% reduction in plant-available metals	NA		
						34% reduction in plant-available metals	NA		
						39% and 64% reduction in labile fraction and shoot concentration of Pb	Formation of Pd phosphate (solubility products of Zn and Cu phosphate are much higher than those of Pb phosphate)	(Usman et al., 2006)	
						86.8% decrease in mobility	Formation of chloropyromorphite	(Hashimoto et al., 2011)	

(continued on next page)

**Table 3 (continued)**

Amendment type	Amendment	TE	Soil condition	Experiment type	QA/QC measures	Dose, %	Effectiveness (compared to control)	Mechanisms/reasons for immobilization	Reference
Others	Phosphoric acid	Al Cd Cr Cu Mn Ni Zn	Sewage effluent irrigated soil	Pot experiment	3 replicates Certified reference materials for each element ANOVA test	1	18.7% decrease in availability 1.4% decrease in availability 45.1% decrease in availability 12.3% decrease in mobility 19.8% decrease in availability 55.8% decrease in availability species	NA	(Shaheen et al., 2017e)
	Sulfur	Cr	Sewage effluent irrigated Mn soil	Pot experiment	3 replicates Certified reference materials for each element ANOVA test	1	9.7% decrease in availability 37.6% decrease in mobility 12.5% decrease in mobility 27.1% decrease in mobility	Sorption of Ni from soil solution; Sorption of Zn from soil solution; reduced mobility	(Shaheen et al., 2017e)
	Potassium humate								

NA: Not available; RCB: Randomized Complete Blocks Design.

in contaminated soils. Understanding the mechanisms and suitability of various clay mineral types in PTE immobilization is important for achieving remediation goals.

#### 4.2.2. Coal fly ash

Also known as pulverized fuel ash, coal fly ash is a byproduct of burning pulverized coal in power generation plants, which is an abundant solid waste worldwide due to issues with managing and disposing huge quantities of it (Ram and Masto, 2014; Seshadri et al., 2013). Important physicochemical properties of fly ash such as favorable pH, high water holding capacity, low bulk density, and the presence of substantial plant nutrients make it a potential soil ameliorant (Pandey and Singh, 2010). Shaheen et al. (2014a) reviewed opportunities and challenges related to using coal fly ash to improve soil and documented significant effects for improving soil quality through remediation as well as plant growth and production. Applying coal fly ash seems to offer significant potential for immobilizing Pb. For example, a greenhouse pot experiment demonstrated that applying coal fly ash significantly reduced soluble and exchangeable Pb (14.7%) in contaminated soil, leading to a significant reduction of Pb in rapeseed plant tissue (66.1%) (Shaheen and Rinklebe, 2015a). Houben et al. (2012) observed that coal fly ash reduced Cd, Zn, and Pb leaching by 32.9%, 41.2%, and 25%, respectively, primarily through increased soil pH.

Elevated soil pH resulting from coal fly ash application is responsible for PTE immobilization in many cases (Shaheen and Tsadilas, 2010; Tsadilas et al., 2009). Mahar et al. (2016) observed 88%–94% immobilization of diethylenetriaminepentaacetic acid (DTPA) extractable Cd in a pot experiment conducted with a soil polluted by zinc smelters and mining. Increasing soil solution pH from ~5.5–7 aided PTE immobilization through precipitation and sorption. Most studies suggest that increased soil pH following coal fly ash application is the major reason for PTE immobilization in soil. However, Janoš et al. (2010) demonstrated that applying coal fly ash effectively reduced Cu mobility in a soil that did not experience a significant pH change. These results imply that increased soil pH is not the only reason for PTE immobilization in soils amended with coal fly ash. A review conducted by Shaheen et al. (2014a) found that the occurrence of constituents such as alumina, calcium oxide, ferric oxide, magnesium oxide, silica, and carbon in coal fly ash may have the potential for PTE retention as those constituents are strong metal sorbents. However, care should be taken when dealing with coal fly ash as it can also be a significant source of PTEs (Shaheen et al., 2015a; Shaheen et al., 2014a). Interestingly, Gu et al. (2011) observed a marked reduction in Cd, Cu, Zn, and Pb uptake by rice plants after applying coal fly ash in both field and pot experiments. This reduction can be explained by in situ immobilization and Si-mediated effects in rice. In situ immobilization was mainly attributed to the conversion of soluble PTEs to less soluble forms such as hydroxides, phosphates, and metal silicates. Increased Si concentration in rice plants blocked the transfer of PTEs to the plants after coal fly ash application by forming co-precipitation with PTEs, indicating Si-mediated effects on PTE phytoavailability and phytotoxicity. A PTE contaminated soil amended with coal fly ash showed 74%–78% and 74%–84% reduction in DTPA-extractable Cu and Pb respectively (Mahar et al., 2016). Adding coal fly ash increased soil pH, thereby immobilizing Cu and Pb, while physical adsorption and precipitation of Pb on coal fly ash surfaces also inhibited Pb mobilization.

By contrast, coal fly ash may not always be effective in immobilizing PTEs because of PTE characteristics, heterogeneity of coal fly ash characteristics, soil type, and other agro-climatic conditions (Ram and Masto, 2014). Nevertheless, coal fly ash itself tends to be enriched in PTEs and thus may pose ecological risks to soil, water, and plants (Ram and Masto, 2014; Shaheen et al., 2014a). Excessive loads of coal fly ash may cause phytotoxicity from PTEs such as B, Mo, and Se (Ukwattage et al., 2013). Application of high doses of coal fly ash may result in accumulation of PTEs in soil, negative affect on soil microbial and enzyme activities, and increase plant PTE uptake (Nayak et al., 2015).

Thus, applying coal fly ash to soils must be done with great caution. Applying coal fly ash together with other amendments such as sewage sludge and clay minerals has also shown better PTE immobilization performance (Shaheen and Tsadilas, 2010; Tomasevic et al., 2013). For instance, applying coal fly ash in combination with kaolinite caused decreased Ni and Zn leachability in a contaminated sediment through solidification and stabilization (Tomasevic et al., 2013). Shaheen and Tsadilas (2010) and Tsadilas et al. (2009) suggested that combined application of coal fly ash with biosolids would be beneficial for remediation of acidic soils containing Pb, Cd, Cu, and Zn due to soil pH changes.

The above discussion may aid in selecting appropriate coal fly ash treatments and/or combined treatments in terms of soil characteristics and coal fly ash properties for immobilizing certain PTEs in soil. Moreover, it is recommended to avoid the application of high dosages to minimize accumulation of various other PTEs in soils.

#### 4.2.3. Liming materials

Liming materials are acid-soluble materials applied to soils primarily to raise the pH of acidic soils. However, liming is also an important tool for minimizing PTE toxicity in soils (Bolan et al., 2003d). Several liming materials, such as carbonates, oxides, and hydroxides of Ca and Mg and many others, have been used to immobilize PTEs with varying degrees of success (Bolan et al., 2003f; Holland et al., 2018). In addition to commonly used liming materials, biological waste (e.g., eggshells, mussel shells, and oyster shells), biochar, red mud, and clay minerals have been recognized as liming materials. The liming effects of these materials have been proven to successfully immobilize PTEs in soils.

Rinklebe and Shaheen (2015) tested different liming materials such as limestone, sugar beet factory lime, and cement kiln dust on Cu mobility in contaminated soil using a pot experiment, and observed reductions in the soluble and exchangeable fraction of Cu of 23.8%, 11.8%, and 6.4% for the three amendments, respectively. The high pH levels (9.1, 8.7, and 12.6, respectively) and higher total CO<sub>3</sub> percentages (98.5, 82.4, and 19.8%, respectively) of the three amendments were responsible for significant reduction in Cu mobility in the studied soil. Increased soil solution pH in the amended soil facilitated Cu immobilization through sorption and precipitation. In another study a reduction in water-soluble Ni and Zn of ~89%–100% were resulted following the application of cement bypass kiln dust, limestone, and sugar beet factory limes in a contaminated floodplain soil (Shaheen et al., 2015a). A study by Shaheen and Rinklebe (2015a) found that soluble and exchangeable Pb was reduced by up to 87%, whereas a relatively lower reduction of Cd (up to 60%) was resulted with the application of above mentioned liming materials. However, increased Cd levels were observed in the carbonate fraction and in rapeseed plants. The excellent immobilization rate for Ni, Zn, and Pb can be explained by increased soil pH and precipitation as carbonates (Shaheen and Rinklebe, 2015a; Shaheen and Rinklebe, 2017). However, Cd was available for plants because Cd-associated carbonates are likely to be released when dissolved in the rhizosphere (Shaheen and Rinklebe, 2015a). Therefore, the risk of Cd mobilization with such liming material may limit their use in soils contaminated with both Pb and Cd.

Liming also directly enhances soil quality by ameliorating soil acidity, thereby aiding crop productivity. A contaminated acidic soil treated with an application of CaO in a pot experiment with Chinese cabbage (*Brassica rapa chinensis*) was tested for PTE immobilization and plant growth (Mahar et al., 2016). Results showed that applying CaO increased soil pH from 5.54 to 8.73, whereas DTPA-extractable Cd, Cu, and Pb concentrations were decreased by 75%–85%, 58%–74%, and 81%–91%, respectively. Consequently, an increased dry biomass yield of Chinese cabbage was also observed; however, the authors warned that applying higher dosages of CaO (e.g., 5%–10% (w/w)) could negatively affect plant growth and might increase PTE phytoavailability

(Mahar et al., 2016). A five-year field experiment revealed that application of lime increased soil pH and reduced the availability, bioaccessibility and leachability of Cu and Cd in ryegrass grown land (Cui et al., 2016a). Although the soil pH was increased at the early stages of the experiment, the soil pH tended to decrease with the time due to the impact of different environmental factors. This is one of the major challenges experience in field experiments. Therefore, under field conditions repeated application of soil amendment is required for effective results.

Immobilization and phytoavailability of Cd, Zn, and Pb in contaminated soil were evaluated after adding CaCO<sub>3</sub> (Houben et al., 2012). Leaching of Cd, Zn, and Pb was reduced by 88.3%, 98.5%, and 57% respectively, whereas following the application of CaCO<sub>3</sub>, PTE concentrations in white lupin (*L. albus L.*) shoots decreased by 82.2%, 87.5%, and 54.5%, respectively (Houben et al., 2012). Like the previous cases, soil pH increases of up to 8 after applying CaCO<sub>3</sub> assisted PTE immobilization through precipitation. It is well known that applying alkaline materials to soil increases soil pH and induces PTE immobilization through several mechanisms. Because of its alkaline nature, these materials reduce H<sup>+</sup> concentration, thereby increasing negatively charged sites in the soil. Consequently, positively charged PTEs can be sorbed onto negative sites (Bolan et al., 2014). In contrast, PTE precipitation in the form of carbonates, hydroxides, phosphates, and oxides at higher soil pH levels may also explain why liming lowered PTE mobility in the soil (Park et al., 2011). Moreover, it has been reported that liming is one of the most important approaches to immobilizing Pb and Cd in soil (Tsadilas, 2000).

Low-grade MgO has also been identified as an economically feasible alternative for stabilizing PTEs in contaminated soils/sediments (Wang et al., 2019b). Applying MgO into a contaminated soil was found to form litharge (PbO) and Pb hydroxide, thus stabilizing available Pb in the soil (Sanderson et al., 2015). Moreover, because MgO acts as a buffering agent within pH range of 9–11, it minimized PTE solubility while avoiding redissolution (Garcia et al., 2004). However, applying larger quantities of MgO may result in mobilization of anionic PTEs, such as As and Mo, and immobilization of beneficial micronutrients such as Fe, Mn, Zn Cu, and B (Holland et al., 2018). Therefore, determining suitable soil qualities and predicting expected soil pH are important considerations prior to lime application. Nonetheless, applying liming materials together with other soil amendments can maximize liming material use efficiency. For instance, Khan and Jones (Jamal Khan and Jones, 2008) documented that applying limestone together with treated sewage sludge raised soil pH and facilitated the formation of insoluble metal complexes, thereby minimizing PTE mobility and phytoavailability. Subsequently, it helped increased tomato biomass production by lessening phytotoxicity due to elevated levels of Cu, Pb, and Zn. Similarly, Ye et al. (2000) reported that applying lime together with manure compost reduced DTPA-extractable Zn and Pb concentrations in acidic tailings while promoting effective growth of two grass species. This was achieved by the limestone neutralizing acidic tailings and the manure providing plant nutrients. These studies thus suggest that combined application of liming materials with appropriate organic amendments may effectively reduce PTE mobility while improving plant productivity.

#### 4.2.4. Metal oxides/red mud

Metal oxides, such as hydroxides, oxyhydroxides, and hydrous oxides of Al, Fe, and Mn, are naturally occurring soil components. These weathering products exist in soils as discrete crystals, mixed gels, and coatings on other particles (Scheinost, 2005). Although they do not exist in large quantities, these products play an important role in soil geochemistry. Because metal oxides have strong sorption and immobilization effects, natural and synthesized oxides and industrial residuals such as red mud have been widely used as stabilization agents to remediate PTE-contaminated soils (Hua et al., 2017). Recent research on the use of red mud as an immobilizer in TE-contaminated soils was

reviewed by Hua et al. (2017). Metal oxides are generally characterized as having an amphoteric nature, small particle size, high surface area with reactive surface sites, and low solubility under common soil pH values (Bolan et al., 2014; Scheinost, 2005). Some of these important properties make them suitable for immobilizing PTEs through mechanisms such as coprecipitation, specific sorption, and formation of inner-sphere complexes.

Gibbsite, boehmite, and diaspore are Al (hydr)oxides that can be found in soil with greater potential for soil remediation. Rajapaksha et al. (2015) observed significant reduction in NH<sub>4</sub>OAc-extractable Pb after applying gibbsite to contaminated soil. However, gibbsite did not effectively immobilize Cu. In contrast, Yang et al. (2015) reported that incorporating gibbsite significantly reduced CaCl<sub>2</sub>-extractable Cu concentrations in Cu-contaminated soil. Despite the natural Al oxides having immobilizing effects, Garcia-Sanchez et al. (2002) reported that synthetic Al(OH)<sub>3</sub> was effective at immobilizing soil As. Synthetic Al (OH)<sub>3</sub> showed higher adsorption capacity (122 mg/g at pH = 5), with an immobilizing effect of approximately 100%, than natural Fe oxyhydroxides and clay minerals. However, in addition to inorganic amendments (e.g., metal oxides) alone, incorporation with organic amendments such as biochar showed enhanced PTE immobilization efficiency (Rajapaksha et al., 2015). Oustriere et al. (2017) reported that applying pine bark chip-derived biochar together with iron grit can effectively immobilize labile soil Cd, Zn, and Pb through increased pH, precipitation-co-precipitation, and various sorption mechanisms.

Iron oxides such as akageneite, feroxyhyte, ferrihydrite, goethite, hematite, lepidocrocite, maghemite, and magnetite are commonly found in soils (Komárek et al., 2013). Iron oxide seems to be more effective at immobilizing As than other PTEs such as Cd, Pb, and Zn. Because As occurs in soils as AsO<sub>4</sub><sup>3-</sup> and AsO<sub>3</sub><sup>3-</sup> oxyanions, most of the amendment previously discussed were not effective at immobilizing As. However, the availability of positive charges on the surfaces of iron oxides facilitates the immobilization of As, Cr, Sb, and other PTEs that occur as anions in soil (Warren and Alloway, 2003). Arsenic adsorption into iron oxides can be explained by ligand exchange of As species for OH<sup>-</sup> and OH<sub>2</sub> groups on the surfaces of iron oxides (Komárek et al., 2013). In addition, Sherman and Randall (2003) reported that adsorption of AsO<sub>4</sub><sup>3-</sup> onto ferrihydrite, goethite, hematite, and lepidocrocite could be mainly attributed to the formation of inner-sphere surface complexes resulting from bidentate corner-sharing between AsO<sub>4</sub> and FeO<sub>6</sub> polyhedra. Inner-sphere surface complexation of As on Fe (oxy)hydroxide may produce a chemically stable form in soil, which was shown by a long-term incubation study demonstrating that adding ferrihydrite (with mixture of gypsum) to contaminated soil significantly reduced the amount of dissolved As for 754 days (Kameda et al., 2017). Fendorf et al. (1997) determined that surface structures of CrO<sup>2-</sup> and AsO<sub>4</sub><sup>3-</sup> had sorbed on goethite using extended x-ray absorption fine structure spectroscopy, where three different surface complexes, based on oxyanion–Fe distances, on goethite were observed for both CrO<sup>2-</sup> and AsO<sub>4</sub><sup>3-</sup>: a) a monodentate complex, b) a bidentate–binuclear complex, and c) a bidentate–mononuclear complex. Because Cr(III) is less mobile in soil, conversion of Cr(VI) to a trivalent oxide or co-precipitation with Fe hydrous oxide reduces Cr mobility and bioavailability in soil (Fendorf, 1995). Industrial iron grit products, which mostly contain Fe<sup>0</sup>, have been extensively studied for contaminated soil remediation. Kumpiene et al. (2006) studied the application of 1% iron grit on As, Cr, Cu, and Zn mobility and bioavailability in contaminated soil. Applying iron grit effectively reduced As and Cr concentrations in leachates by 98% and 45%, in soil pore water by 99% and 94%, and in plant shoots by 84% and 95%, respectively. In contrast, elevated Cu and Zn concentrations were observed in plant shoots in treated soil, which indicated increased Cu and Zn bioavailability. Nevertheless, Yang et al. (2015) reported that applying ferrihydrite significantly reduced CaCl<sub>2</sub>-extractable Cu concentrations in Cu-contaminated soil. Houben et al. (2012) documented that among other soil amendments, such as bentonite, bone meal, CaCO<sub>3</sub>, fly ash, iron grit, and manure, iron grit was

the most efficient at reducing Pb leaching. More interestingly, applying iron grit effectively removed DOC from solution through newly formed iron oxides, in addition their Pb sorption capacity. Because DOC increases Pb mobilization in soils, removing DOC further explains the greater immobilization of Pb seen with oxidized iron grit.

Manganese oxides are another important scavenger of PTEs in soils. Birnessite, cryptomelane, hausmannite, manganite, pyrolusite, and todorokite are Mn oxides commonly occurring in soil environments (Komárek et al., 2013). Manganese oxides have proven to be an efficient sorbent for Pb, Co, Cu, Cd, and Zn, and have exhibited much greater effectiveness at immobilizing Pb than Fe oxides (Dong et al., 2000; Feng et al., 2007). This could be attributed to Mn oxides having large specific surface areas and negative surface charges. Applying manganese oxide to agricultural soil polluted with Pb had no effect on Cd and Zn leaching, whereas As, Cu, Pb, and Sb leaching was significantly decreased (Ettler et al., 2015). Immobilization efficiency was even more pronounced for As, Cu, Pb, and Sb under acidic conditions, and Cd and Zn sorption were found to be highly pH dependent and less effective under Mn oxide amendments (Della Puppa et al., 2013; Ettler et al., 2015). However, remediation of PTEs such as As, Co, and Cr with Mn oxides must be done with special care as they are redox-sensitive elements (Komárek et al., 2013). In soil systems, As(III) and Cr(III) can be oxidized into As(V) and Cr(VI) while Mn(IV) is reduced to Mn(II) (Tang et al., 2014; Tournassat et al., 2002). This may result in dissolving Mn oxides through oxidation/reduction processes, known as As (III)/Cr(III) oxidation, coupled with reductive dissolution of Mn oxide, especially at low pH levels. However, the resultant As(V) is less toxic and Cr(VI) is more toxic and mobile in the soil. Furthermore, As can be immobilized by Mn oxides by forming a highly insoluble mineral, Mn<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O, at low pH, and through co-precipitation as MnHA<sub>0.8</sub>SO<sub>4</sub>·8H<sub>2</sub>O (Porter et al., 2004; Tournassat et al., 2002). Hence, As can be immobilized using Mn oxides, whereas Mn oxide treatments cannot effectively immobilize Cr.

#### 4.2.5. Phosphates

Phosphate-containing amendments are added to soil to improve soil fertility or remediate contaminated soil. The PTE immobilization capacity of phosphate amendments has been extensively studied and well documented in the literature (Bolan et al., 2003c; Bolan et al., 2003g). Apatites, hydroxyl apatites, diammonium phosphate (DAP), phosphate-based salts, phosphoric acid, and phosphate rocks (PR) are commonly used phosphate-containing amendments that have been successfully used for PTE immobilization in contaminated soils. It is well known that Pb immobilization with P amendments is strongly effective due to the formation of stable Pb phosphates, such as pyromorphite. Applying phosphate amendments leads to precipitation of pyromorphites, Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>X, where X = F, Cl, Br, or OH, which are highly insoluble under a wide range of pH and Eh values in a natural environment (Kumpiene et al., 2008). A field study at a Pb-contaminated site showed that phosphate amendments significantly reduced Pb mobilization through formation of chloropyromorphite [Pb<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>] (Cao et al., 2002). Pyromorphite formation through the application of inorganic phosphate compounds to Pb contaminated soils was confirmed using XAS (Hashimoto et al., 2011); however, the efficiency of transformation from original soil Pb species (e.g., PbCO<sub>3</sub>) to pyromorphite was up to 30% of total Pb, which likely depended on soil properties (Hashimoto et al., 2009b). Moreover, ion exchange is also known as being effective at immobilizing Pb in contaminated soils. In a multi-metal contaminated soil, PR showed the highest affinity for Pb (immobilized up to 78.3%), followed by Cu and Zn (Cao et al., 2004). Formation of fluoropyromorphite (Pb<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>F<sub>2</sub>) was identified as the main mechanism for Pb immobilization, whereas Cu and Zn were immobilized by surface adsorption or complexation. A similar affinity trend was observed by Fang et al. (2012) for Pb, Zn, and Cu with PR, triple superphosphate fertilizer, and combination of the two amendments.

He et al. (2013) observed significant reduction in water soluble Pb

(72%) and Cd (90%) after applying nano-hydroxyapatite to an artificially contaminated soil. Immobilizing Cd was explained by isomorphic substitution of Cd with Ca in nano-hydroxyapatite, which might be attributed to Cd and Ca having close ionic radii. Immobilization of Pb was attributed to the precipitation of new metal phosphate minerals identified by XRD analysis, such as phosphate hydroxide ( $Pb_xCa_{10-x}(PO_4)_6(OH)_2$ ), lead dihydrogen phosphate, pattersomite, and lead phosphate. On the contrary, Shaheen et al. (2017e) warned that applying triple superphosphate (TSP) and PR to contaminated soils could increase plant Cd uptake. They observed increased Cd uptake by sorghum after applying TSP and PR, which they ascribed to the inherent high Cd content and high acidity of TSP and PR. Decreased soil pH resulting from the application of these phosphate amendments caused an increase in Cd solubility, whereas high levels of total Cd in TSP and PR released a soluble form of Cd, thereby increasing plant Cd uptake. Care should thus be taken when selecting phosphate amendments and dosages that are appropriate for the target PTEs. However, to solve the issue, the application of gypsum to these soils would be a viable option to immobilize Cd in soil (Qayyum et al., 2017). Application of monocalcium phosphate decreased Pb mobility while increasing As mobility in contaminated soil, which can be explained by the close chemical similarity between  $PO_4^{3-}$  and  $AsO_4^{3-}$  ions leading to the partial substitution of the latter by the former after the phosphate amendment was applied (Shaheen and Tsadilas, 2015). However, simultaneous immobilization of Pb and As can be achieved by applying a mixture of monocalcium phosphate and ferrous sulfate. Cui et al. (2010) conducted a similar study and observed the same effects for Pb and As mobility with calcium magnesium phosphate, PR, and single superphosphate combined with ferrous sulfate. Increased As mobility with phosphate treatments can be explained by competition between  $PO_4^{3-}$  and As ions, which led to the desorption of adsorbed As, increasing As mobility (Shaheen and Tsadilas, 2015). Thus, we do not recommend applying phosphate amendments to As contaminated soil. Moreover, as some phosphate amendments such as RP act as sources of some PTEs, combined application with materials such as gypsum might be an efficient way to remediate contaminated soils while improving crop production.

## 5. Evaluating the feasibility of soil remediation using soil amendments as immobilization agents

A comprehensive comparison of all potential soil amendments and their applicability and efficacy to specific PTEs is needed for evaluating the feasibility of soil remediation using the immobilization technique.

We reviewed > 60 published article (included in Table 2 and 3) and analyzed statistically the published results to compare the efficiency of different soil amendment including animal wastes, biochar, compost, clay minerals, liming materials, metal oxides, and phosphates on immobilization of Pb, Cd, Zn, and Cu (Fig. 4). We used data present the effects of amendments on the metal bio-accessibility, exchangeable fraction, labile fraction, leaching, phytoavailability, and water-soluble fraction.

Based on the median values presented in Fig. 4, we can extract that the amendments immobilized Pb efficiently (with an immobilizing percent  $\geq 50\%$ ); however, biochars, phosphates and liming materials showed higher efficacy ( $> 85\%$ ) for Pb immobilization than compost, clay minerals, and metal oxides ( $< 65\%$ ). On other hand, the efficiency of these amendments for immobilization Cd was lower than Pb and varied from 55 to 60% with animal wastes, liming materials, and biochar to 15% with compost. The biochar and compost immobilized Cu efficiently (with an immobilizing percent  $\geq 80\%$ ); followed by metal oxides (55%), liming materials (30%), clay minerals (25%), and phosphates (15%). On other hand, the efficiency of the amendments for immobilization Zn varied from 70 to 77% with animal wastes, liming materials, and biochar to 25% with phosphates.

The above results regarding the application of soil amendments to

contaminated soils indicated that, except for a few cases, most organic and inorganic soil amendments can be used as PTE immobilization agents. However, biochars, phosphates, and liming materials are more recommended for remediation of Pb contaminated soils; biochars and compost for Cu contaminated soils; biochar, animal wastes, and liming materials for treatment of Cd and Zn contaminated soils. On the other side, special attention must be paid in case if using amendments such as biosolids, municipal solid waste, and coal fly ash, because these materials may contain organic or inorganic contaminants that could negatively affect soil quality. Therefore, it is highly recommended to fully characterize potential source materials used for immobilization PTEs in contaminated soils.

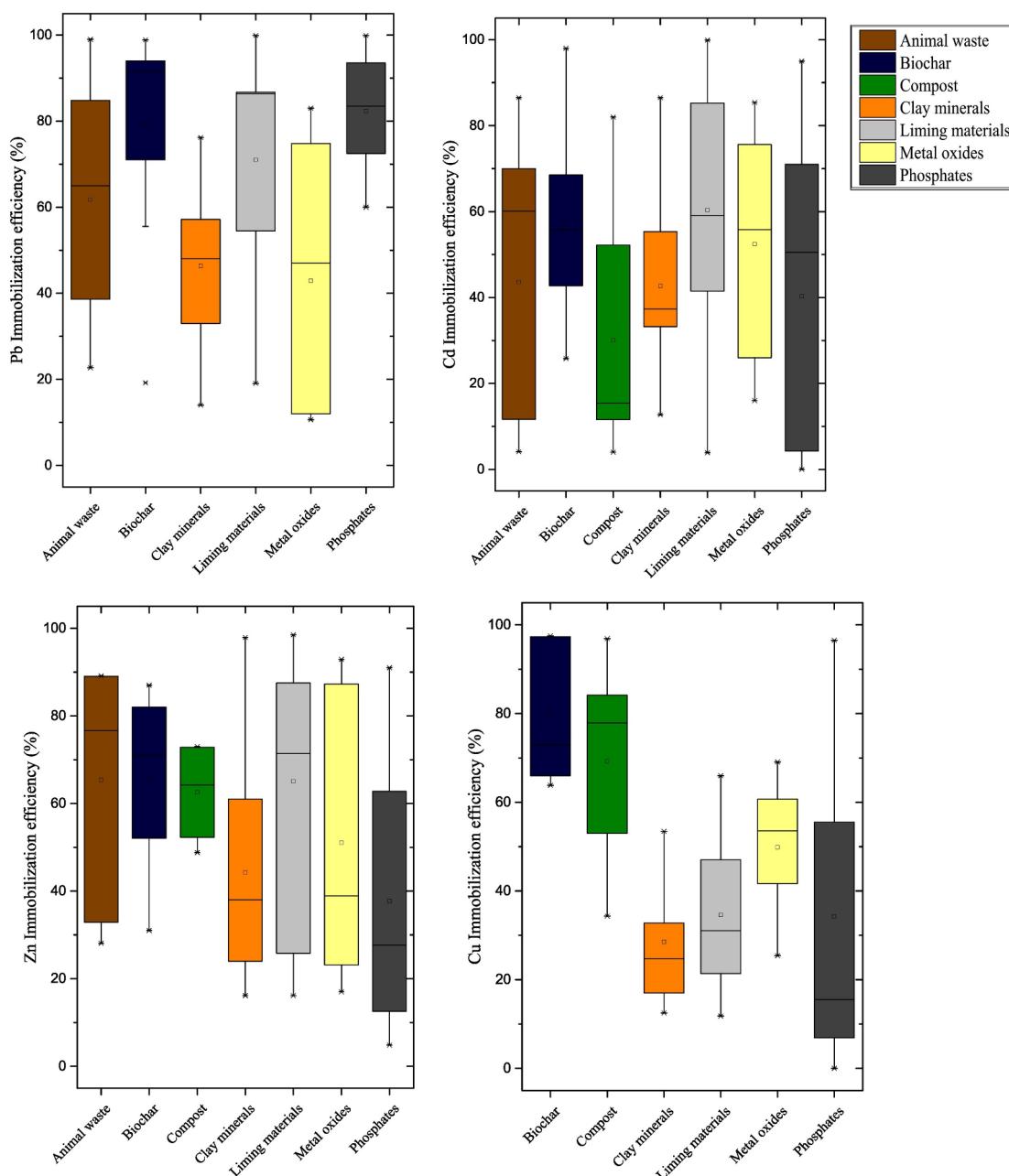
An amendment's economic feasibility is also an important consideration for material selection. Natural residues or waste materials are more cost effective than synthetic stabilizing agents and have shown better PTE immobilization performance in soils. Thus, such low cost, abundant, and environmental friendly materials are recommended for immobilization of PTEs in soils from both economic and environmental points of view.

In conclusion soil amendments such as biochar, compost, animal wastes, phosphates, and liming materials are recommended for remediation of PTEs contaminated soils, because of their high efficacy as immobilizing agents and soil conditioners, low cost, applicability, and also due to their economic feasibility.

## 6. Conclusions and perspectives for future research

We reviewed the potential immobilization of PTEs in soil using various soil amendments to minimize the bioavailability and toxicity of these pollutants. Potentially toxic elements can be released to the environment, from both natural and anthropogenic sources have caused varying levels of soil contamination and reduced productivity of arable land worldwide. Several remediation practices have been adopted to reduce the hazardous effects of PTEs and restore contaminated soil ecosystem. Applying soil amendments is considered one of the easiest to adopt and most cost-effective in situ remediation techniques to improve soil quality through PTE immobilization. A range of organic and inorganic soil amendments, such as animal wastes, biochar, biosolids, compost, clay minerals, coal fly ash, liming materials, metal oxides, and phosphates, are commonly used as PTE immobilizing agents. However, some important aspects must be considered when selecting a suitable immobilizing agent for any practical application.

Moreover, it is crucial to understand soil conditions and target PTE behaviors. Soil physicochemical properties such as pH, Eh, CEC, EC, and OM content directly correlate with PTE mobility and availability; therefore, these soil characteristics may provide guidance for selecting the proper amendment with higher efficiency. At the same time, identifying the target PTE (for example whether it is a cation or anion) and its behavior under different environmental conditions should be done in parallel for effective remediation. Understanding the various interactions and mechanisms between a target PTE and immobilizing agent is crucial for managing PTE contamination in the short and long terms. Soil amendments can immobilize PTEs through various mechanisms such as ion exchange, precipitation, complexation, and adsorption reactions. These processes redistribute PTEs from a soil solution to solid particles, thus limiting bioavailability and leachability to ground water. Given that the various physicochemical properties of soil amendments could reduce PTE mobility in soils, there is not a single amendment type that could be generally applied to remediate all contaminated soils. Moreover, no one amendment, mechanism, or application rate holds true for remediating all PTEs in all soils. Thus, selecting soil amendments for remediation of PTE-contaminated soils requires one to account for the types of PTEs present in the soil, the sources and physicochemical properties of soil amendments, and the stability of immobilized PTEs in soil. Selection of soil amendments is critical especially in multi-PTE contaminated soils. For example, while the



**Fig. 4.** Effects of different soil amendments on immobilization of Pb, Cd, Zn, and Cu. Immobilization is the reduction of potentially toxic elements in terms of bioaccessibility, exchangeable fraction, labile fraction, leaching, phytoavailability, and water-soluble fraction (detailed data are available in the supplementary material file and Table S2).

application of phosphate compounds is very effective in the immobilization of PTEs such as Pb and Zn in soils, it can facilitate the mobilization of PTEs such as As and Sb. Therefore, it is important to use a combination of amendments in multi-PTE contaminated soil. Under long term field condition, different environmental phenomena such as rainfall, ageing, weathering, acid deposition and temperature fluctuation are some of the challenges to achieve remediation goals. With these environmental stresses long-term sustainability of amendments in field conditions may decrease over time and repeated applications is required for full effectiveness.

One of the major drawbacks associated with immobilization techniques is that, although PTEs are immobilized after applying a soil amendment, the total PTE concentration remains unchanged. Consequently, they could be mobilized and become bioavailable again over time under changing environmental conditions. Therefore,

attaining effective remediation efficiency must be accompanied by continuous monitoring to avoid undesired PTE mobilization or leaching.

Despite increasing research of application of soil amendments to contaminated soils, many areas are yet to be developed. For example, (im)mobilization of PTEs in amended soils can be examined using advanced spectroscopic techniques combined with sequential extraction, which may provide insights into PTE mobility mechanisms. We have identified some knowledge gaps, which will require further investigation in future studies. For instance, elucidating PTE temporal kinetics and determining factors under diverse soil conditions may assist in comprehensive understanding of processes determining soil PTE dynamics. So far, most research on the use of soil amendments to immobilize PTEs in soil have mainly focused on laboratory and greenhouse experiments, plot trials, or leaching tests, and have mostly been

short-term studies. Results from these short-term experiments should thus be verified by field studies to confirm long-term stability of immobilized PTEs in amended soils. Field experiments allow us to evaluate all natural processes affecting PTE mobility, such as meteorological changes, which we cannot produce in laboratory studies. Additionally, soil microorganisms play a vital role in PTE mobilization and immobilization in different soil environments; therefore, it is important to study changes in microbial activity, abundance, diversity, and processes for a range of soil amendments with respect to PTE immobilization, especially in wetlands and reduced soil environments. It is also important to examine how amendments, soil components, and PTEs interact using advanced spectroscopic and microscopic techniques to better understand the underlying processes and mechanisms. Because some PTE immobilizers such as biosolids can also act as PTE sources in soils, it is crucial to develop advanced treatment techniques to eliminate unnecessary metals in amendments. Lastly, regarding the efficiency of soil amendments, modifying soil amendments through various physicochemical processes would be important for improving their ability to immobilize PTEs.

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## Appendix A. Supplementary data

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