### ORIGINAL PAPER

# The role of biochar, natural iron oxides, and nanomaterials as soil amendments for immobilizing metals in shooting range soil

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Abstract High concentration of toxic metals in military shooting range soils poses a significant environmental concern due to the potential release of metals, such as Pb, Cu, and Sb, and hence requires remediation. The current study examined the effectiveness of buffalo weed (*Ambrosia trifida* L.) biomass and its derived biochars at pyrolytic temperatures of 300 and 700 °C, natural iron oxides (NRE), gibbsite, and silver nanoparticles on metal immobilization together with soil quality after 1-year soil incubation. Destructive (e.g., chemical extractions) and nondestructive (e.g., molecular spectroscopy) methods

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were used to investigate the immobilization efficacy of each amendment on Pb, Cu, and Sb, and to explore the possible immobilization mechanisms. The highest immobilization efficacy was observed with biochar produced at 300 °C, showing the maximum decreases of bioavailability by 94 and 70 % for Pb and Cu, respectively, which were attributed to the abundance of functional groups in the biochar. Biochar significantly increased the soil pH, cation exchange capacity, and P contents. Indeed, the scanning electron microscopic elemental dot mapping and X-ray absorption fine structure spectroscopic (EXAFS) studies revealed associations of Pb with P (i.e., the formation of stable chloropyromorphite  $[Pb_5(PO_4)_3Cl])$  in the biomass- or biochar-amended soils. However, no amendment was effective on Sb immobilization.

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### Introduction

Heavy metal pollution of soils is a matter of concern worldwide. Anthropogenic activities, such as the military training, mining industry and treatment of metal ores, waste incineration, road transport, and the use of fertilizers and agrochemicals, lead to excessive concentrations of heavy metals in soils. Particularly, high concentrations of toxic metals in military shooting range soils are critical environmental concern, due to the potential releases of Pb, Cu, and other metalloids such as Sb (Dermatas et al. 2006; Cao et al. 2008; Ahmad et al. 2012a). When used bullets enter into the soil, Pb is readily released, and subsequently transformed into a wide range of Pb species, including Pboxides, Pb-hydroxides, Pb-carbonates, Pb-sulfates, and Pb-carboxylates (Ahmad et al. 2012b; Hashimoto 2013). These metals and metalloids do not undergo microbial or chemical degradation, and their total concentration remains unchanged for a long time in soils (Bolan et al. 2014: Adriano et al. 2004).

The utilization of most traditional remediation practices, including soil washing, excavation, and landfilling, is unfeasible on a large scale, due to environmentally disruptive and cost-prohibitive behaviors (Bolan et al. 2014). Due to these concerns, the need has arisen for cost-effective soil remediation techniques as alternatives, such as in situ immobilization technologies, in general through the application of soil amendments (Mulligan et al. 2001; Almaroai et al. 2014; Tsang et al. 2014; Hettiarachchi and Pierzynski 2004). The application of such soil amendments does not alter the total metal concentration, but does reduce the mobility and toxicity of metals. The key immobilizing chemistries involve (ad)sorption, precipitation, complexation, and redox reactions (Adriano et al. 2004; Porter et al. 2004). Until now, various amendments including phosphate compounds (Ma et al. 1995; Bolan et al. 2003), liming materials (Ok et al. 2007, 2011; Lim et al. 2013), organic materials (Park et al. 2011; Brown et al. 2003), and metal oxides (Vithanage et al. 2007; Almaroai et al. 2014) have been examined to immobilize heavy metals in contaminated soils. However, few studies have simultaneously compared the effectiveness of several candidate amendments with different properties for metal immobilization under consistent examining conditions. Biochar, a material obtained from pyrolysis of biomass, has recently gained interest as an alternative soil amendment for the remediation of metal-contaminated soils (Ahmad et al. 2014c). Remediation of contaminated soil using silver, iron, and aluminum nanomaterials is also becoming attractive treatment technology (Karn et al. 2009). Hence, the objectives of this study are (1) to evaluate and compare the effectiveness of biochar, natural iron oxide, and nanomaterials on metal immobilization for the shooting range soils, (2) to investigate soil quality changes accompanied by the application of different amendments, and (3) to predict the possible mechanisms involved in metals immobilization using chemical extractions and spectroscopic analysis.

#### Materials and methods

Soil collection and characterization

Soil was collected from a military shooting range located in Gangwon-do, Korea. The soil was air-dried, and sieved through a 2-mm stainless sieve. The soil was characterized for selected physicochemical properties.

The total heavy metal contents (Pb, Cu and Sb) in the soil were determined by the USEPA method 3051A using a microwave-assisted digestion unit (MARS, HP-500 plus, CEM Corp., USA) and an inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 7300 DV, Perkin Elmer, USA). Soil organic matter content was determined by the Walkley and Black titration method (1934). The total C and N in the soil sample were measured by an elemental analyzer (vario MAX CN, Elementar, Germany). The soil texture was also determined by the hydrometer method (Gee and Or 2002).

#### Soil amendments and incubation experiment

Buffalo weed (*Ambrosia trifida* L.) was collected as biomass (BM) and its biochar produced at 300 (BC300) and 700 °C (BC700). Natural iron oxide (NRE), gibbsite (GINP), and silver nanomaterial (AgNP) were also used as amendments. Preparation of buffalo weed biochars (i.e., BC300 and BC700) was described in our previous paper (Ahmad et al. 2014b). Briefly, the dried BM was pyrolyzed at 300 °C and at 700 °C under a limited supply of air, at the rate of 7 °C min<sup>-1</sup> for 3 h. Samples of NRE were collected from northwestern Sri Lanka (8°14′50″N and 79°45′45″E). The silica grains of the NRE were completely covered by amorphous coating with variable charge sites of >AlOH and >FeOH, showing a strong affinity for heavy metals, and it has previously been used to immobilize heavy metals and metalloids, including As, Pb, and Sb (Almaroai et al. 2014; Vithanage et al. 2013; Rajapaksha et al. 2011). The GINP was synthesized using 1 M AlCl<sub>3</sub> and 6 M NaOH at pH 4.6 following the method described by Kumara et al. (2010). The AgNP used in this study was the bacteriamediated metallic-silver-nanoparticles, achieved from the Department of Water Management, A.N. College, India. The detailed procedure of the AgNP synthesis and its characteristics are given by the published study of Sharma et al. (2010).

Each amendment was applied to the prepared soil on a weight basis, either at 5 % for BM and biochar, or at 0.1 % for iron oxides and nanomaterials, and then the soil-amendment mixtures were placed in highdensity polyethylene bottles for 1 year at 25 °C, in an automated incubator (MIR-554, SANYO Electronic, Co., Ltd., Tokyo, Japan). All treatments were examined in triplicate, and the soil without any amendments was also included in the experiment batch as the control. Water content of the soil mixture in the incubation bottles was maintained at 70 % waterholding capacity throughout the incubation period.

#### Chemical analyses and thermodynamic modeling

After the incubation period, the soil pH and EC were measured electrometrically, at a soil/water ratio of 1:5. Exchangeable cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ , and  $Na^+$ ) in the soil were analyzed using an ICP-OES after 1 M ammonium acetate extraction, and the cation exchange capacity (CEC) of the soil was also calculated by the Brown's method (NIAST 2000).

Changes in the active soil organic carbon (SOC) in response to the amendments were determined by reacting with dilute potassium permanganate (0.02 M KMnO<sub>4</sub>) (Weil et al. 2003), followed by measurement of the reduction in absorbance at 550 nm, using an UV/visible spectrophotometer (UV-1800, Shimadzu, Japan).

The toxicity characteristic leaching procedure (TCLP) was used to determine the leachability of metals, after incubation of the amended soils (Ahmad et al. 2012b; Cao and Dermatas 2008). Specifically, the TCLP extracting solution No. 1 (pH 4.93) was used. Twenty milliliters of the extracting solution was added to a polypropylene tube containing 1 g of soil, and subsequently inverted for 18 h at 30 rpm. After this, the supernatant was filtered using Whatman No. 42 filter papers ( $2.5 \mu m$ ), and Pb, Cu and Sb in the filtrates were analyzed using an ICP-OES.

The water-soluble anion concentrations were determined at 1:10 ratio of soil/water suspensions, equilibrated for 24 h. The supernatants were filtered and analyzed for anions (NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, and Cl<sup>-</sup>) by an ion chromatography (Metrohm Compact IC-861, Switzerland), cations (Al, Ca, Mg, K, Na, Fe, Pb, Cu, and Sb) by an ICP-OES, and dissolved organic carbon (DOC) by total organic C analyzer (TOC-ASI, Shimadzu, Japan). Heavy metal speciations in the aqueous phase were evaluated by thermodynamic equilibrium modeling. Visual MINTEQ model (ver. 3.0) was used to predict the possible precipitates of Pb and Cu in the treated and untreated soils. The input parameters (anionic and cationic concentrations, and DOC content) are given in Table S1, and the model was run at 25 °C and a CO<sub>2</sub> pressure of  $10^{-3.4}$  atm, using fixed pH values measured in aqueous suspensions. Saturation index (SI) values were also used to predict the possible theoretical metal ion precipitates (Hashimoto 2013).

SEM-EDX mapping and synchrotron-based X-ray absorption fine structure (XAFS) spectroscopy

Scanning electron microscopy (SEM) images and elemental dot mapping of Si, Al, Fe, Mg, Ca, P, K, and Pb were obtained using SEM-EDX (Hitachi S-4800 with ISIS 310, Japan), to correlate the metal bound phases.

The mechanism of heavy metal immobilization in soils was investigated using a synchrotron-based X-ray absorption fine structure (XAFS) spectroscopy. These XAFS spectroscopic investigations were carried out only for Pb speciation due to low levels of Cu and Sb in the soil. The speciation of Pb in the amended and control soils was revealed using a synchrotronbased XAFS spectroscopy at the beam line 7D in the Pohang Light Source (PLS-II, Korea). The EXAFS spectra were collected in a fluorescence mode at room temperature across the Pb L-III absorption edge at 13035 eV, using a Si(111) double-crystal-monochromator. The following Pb reference standards were used: massicot (PbO), plattnerite (PbO<sub>2</sub>), cerussite (PbCO<sub>3</sub>), hydrocerussite (Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>), Pb-phosphate (PbHPO<sub>4</sub>), Pb-acetate ((CH<sub>3</sub>COO)<sub>2</sub>Pb), Pbcitrate (C12H10O14Pb3), Pb-oxalate (PbC2O4), Pb-hydroxide (Pb(OH)<sub>2</sub>), chloropyromorphite (Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl), and Pb sorbed to birnessite, gibbsite, goethite, humic acid, and kaolinite. The Athena software ver. 0.8.061 (Ravel and Newville 2005) was used to analyze spectral data. The  $\chi(k)$  function was employed to isolate the scattering portion of the spectra. The k-space up to 11  $Å^{-1}$  was used for the  $k^2$ -weighted EXAFS spectra. The EXAFS data were subjected to linear combination fitting (LCF) analysis using a combination of up to three reference standards to quantitatively estimate the Pb speciation. A fitting range of 2–10  $\text{\AA}^{-1}$  was used, and the goodness-of-fit was based on the R-factor (normalized sum of the squared residuals of the fit) and reduced  $\chi^2$  values.

### Statistical analysis

The statistical analyses were done by the Statistical Analysis System (SAS; ver. 9.3, Cary, NC, USA). The means of three replicates were subjected to one-way analysis of variance (ANOVA), and the significant differences among the different treatments at a significance level of 0.05 were determined using Tukey's honestly significant difference (HSD). The coefficient of determination ( $R^2$ ) and Pearson's correlation (r) between the various parameters were also calculated.

#### **Results and discussion**

#### Physicochemical properties of the soil

The soil was a sandy loam (67 % sand, 27 % silt, and 6 % clay) having a pH value of 8.00. Exchangeable  $Ca^{2+}$  (1.19  $cmol_{(+)} kg^{-1}$ ),  $Mg^{2+}$  (1.27  $cmol_{(+)} kg^{-1}$ ), and  $K^+$  (0.14  $cmol_{(+)} kg^{-1}$ ) of the soil were lower than the typical values of Korean upland soils, 5.0, 1.5, and

0.5–6.0  $\text{cmol}_{(+)}$  kg<sup>-1</sup>, respectively (Jo and Koh 2004). The value of CEC was 2.72  $\text{cmol}_{(+)}$  kg<sup>-1</sup>.

The total Pb, Cu, and Sb concentrations in the soil were 17468, 1168, and 164 mg kg<sup>-1</sup>, respectively. The total Pb in the soil exceeded (~25 times higher) the Korean regulatory warning levels for shooting range soils at 700 mg kg<sup>-1</sup> (MOE 2010). Even if the total Cu and Sb contents did not exceed the regulatory levels for military sites (2000 mg kg<sup>-1</sup>), they appeared to exceed the standard warning level of Cu (>150 mg kg<sup>-1</sup>) and Sb (>5 mg kg<sup>-1</sup>) regulated for agricultural soil. These findings indicated that the selected soil is severely contaminated with Pb, Cu, and Sb, and urgent for remediation.

Effects of amendments on soil chemical properties

The BCs (particularly, the BC700) significantly increased the soil pH due to the alkaline mineral composition (Ahmad et al. 2014b), while other amendments did not show any effect on soil acidity (Fig. 1a). Among the amendments examined, organic amendments (BM and BCs) increased the soil EC and CEC (Fig. 1b, c). The water-soluble  $PO_4^{3-}$  content was negligible in the control and inorganic amendmentapplied soils (i.e., NRE, GINP, and AgNP). This may be due to  $PO_4^{3-}$  precipitation in the control soil or strong interaction between P and Fe or Al sites in the amended soils (Almaroai et al. 2014). The addition of organic amendments (BM and BCs) increased the water-soluble  $PO_4^{3-}$  content, which indicated the release of available  $PO_4^{3-}$  from BM and BCs into the soil. The DOC content in NRE (21. 45 mg kg<sup>-1</sup>)-, GINP (17.97 mg kg<sup>-1</sup>)-, and AgNP (26.60 mg kg<sup>-1</sup>)-amended soils was lower than the control (32.83 mg  $kg^{-1}$ ). However, the BM, BC300, and BC700 increased the DOC contents by 7.00, 9.30, and 9.20 times higher than control soil, which could be due to the high organic compounds in these amendments. The addition of BM, BC300, and BC700 significantly increased the SOC content from 149.16 mg kg<sup>-1</sup> to 309.11, 624.07, and 348.58 mg kg<sup>-1</sup>, respectively (p < 0.05) (Table 1). This is in good agreement with previous studies, which showed an increase in biologically active soil carbon with BC amendments (Chan et al. 2007; Ahmad et al. 2012c). For example, Ahmad et al. (2012c) showed an increase in SOC by 30.5 % with BC amendments, compared to the unamended soil. Active soil carbons play an important role in soil biodiversity, as well as in the stabilization of



Fig. 1 Changes of (a) pH, (b) electrical conductivity (EC), and (c) cation exchangeable capacity (CEC) in the contaminated shooting range soil amended with natural iron oxide (NRE), gibbsite nanoparticle (GINP), silver nanoparticle (AgNP), biomass (BM), and its biochars produced at 300 (BC300) and 700 °C (BC700). *Error bars* represent the standard deviation of three replicates. The *same letters* above *each bar* indicate no difference at a 0.05 significance level

soil structure (Jastrow et al. 2007). Overall, compared to the inorganic amendments, the organic amendments appeared to be more effective in enhancing the soil chemical properties.

Availability and leachability of metal(loid)s

The addition of all amendments significantly reduced NH<sub>4</sub>OAc-extractable Pb (p < 0.05) (Fig. 2). The extractability of Pb in the soils decreased by 13.6 % with NRE, 9.8 % with GINP, 5.5 % with AgNP, 35.5 % with BM, 94.7 % with BC300, and 92.6 % with BC700, compared to the control soil. The greatest decline in extractable Pb was obtained with BC300 and BC700, indicating that the addition of BCs is more effective for Pb immobilization than the other amendments tested. With the exception of GINP, all the amendments decreased NH<sub>4</sub>OAc-extractable Pb, maximum decrease of 81.35 % in NH<sub>4</sub>OAc-extractable Cu was observed in the soils amended with BC300.

The TCLP extraction showed that the control soil exceeded the critical level (5 mg Pb  $L^{-1}$ ), and this implied that the soil would be characterized as hazardous waste by the TCLP (EPA/530/SW-846 1991) (Fig. 3). Also, high concentrations of both total Pb (17468 mg kg<sup>-1</sup>) and TCLP-Pb (5190 mg kg<sup>-1</sup>) signified that this shooting range soil is strongly contaminated with Pb and would require Pb-clean up or special management practices. The applications of BM, BC300, and BC700 decreased TCLP-extractable Pb by 8.1, 77.2, and 74.7 %, respectively, compared to the control soil (Fig. 3).

The BC300 and BC700 decreased the NH<sub>4</sub>OAcand TCLP-extractable Pb and Cu, but not the Sb (Fig. 3). In soil solution, Sb mainly exists as oxoanions Sb(OH)<sub>6</sub><sup>-</sup> (Filella et al. 2009; Okkenhaug et al. 2013), and repulsive electrostatic interactions between Sb anions and negatively charged surfaces of soil/ biochar particles may result in desorption of Sb from the soil. Further, adding PO<sub>4</sub><sup>3-</sup>-rich amendments to soil can enhance the desorption of Sb due to the competition between negatively charged PO<sub>4</sub><sup>3-</sup> ions and Sb species for available sorption sites (Okkenhaug et al. 2013; Uchimiya et al. 2012). Similarly, recent **Table 1** Changes of dissolved organic carbon (DOC), active soil organic carbon (SOC), and water-soluble  $PO_4^{3-}$  contents in the contaminated shooting range soil amended with natural

iron oxide (NRE), gibbsite nanoparticle (GINP), silver nanoparticle (AgNP), biomass (BM), and its biochars produced at 300 (BC300) and 700 °C (BC700)

Amendments	DOC (mg kg <sup>-1</sup> )	SOC (mg kg <sup><math>-1</math></sup> )	$PO_4^{3-} (mg \ kg^{-1})$		
Control	32.83c	149.16c	N.D		
NRE	21.45c	129.99c	N.D		
GINP	17.97c	161.76c	N.D		
AgNP	26.60c	146.42c	N.D		
BM	230.10b	309.11b	3.89b		
BC300	305.50a	624.07a	79.96a		
BC700	301.95ab	348.58b	70.72a		

Different lower case letters in each row indicate significant differences at p < 0.05 among means of various treatments *N*.*D* not detectable

studies indicated Sb mobility after application of several amendments (biochars, lime, manure, etc.), which was attributed to increase in pH with the addition of amendments (Klitzke and Lang 2009; Uchimiya et al. 2012). Among all the amendments used in the study, BC300 was the most effective in immobilizing Pb and Cu in the soil, and this could be explained by the abundance of functional groups of BCs, as well as the high P contents (Table 1). A recent study by Uchimiya et al. (2012) showed the retention of heavy metals by carboxyl functional groups of BCs. Pb and Cu cations are able to form strong complexes with carboxyl functional groups on the surfaces of biochars (Uchimiya et al. 2012). The ion exchange capacities of BC are high, compared to those of the other amendments. Pb and Cu immobilization can be explained by the precipitation of Pb and Cu as phosphate, carbonates, and hydroxides, mainly under increases in soil pH and CEC (Moon et al. 2013a, b). This study showed that the TCLP-extracted Pb contents are negatively correlated with the soil pH (r = -0.90, p = 0.005), water-soluble PO<sub>4</sub><sup>3-</sup> content (r = -0.987, p < 0.0001), DOC (r = -0.886, p =0.008), and CEC (r = -0.92, p = 0.003) (Fig. 4 and Fig. S1). Increase in soil pH leads to the formation of stable metal species, which are not easily soluble or leachable to the environment (Cao et al. 2011; Lim et al. 2013; Moon et al. 2013b). Strong correlations of Pb and Cu mobility with soil pH and CEC indicated that precipitation and ion exchange could be the possible mechanisms of metal immobilization in shooting range soil. Specifically, the high pH and CEC induced by the BCs (Fig. 1) resulted in decreased availability and leachability of Pb and Cu. From this study, it can generally be concluded that better in situ stabilization may be achieved with the addition of BCs than with the other amendments. Further insight into the metal immobilization mechanism induced by BC application is studied using thermodynamic modeling, elemental mapping, and EXAFS spectroscopy.

# Thermodynamic modeling, elemental mapping, and EXAFS interpretation

The possible metal minerals in the control and amended soils predicted by the visual MINTEQ model are presented in Table 2. In the control soil, all possible Pb species, except Pb(OH)<sub>2</sub>, were undersaturated (SI value <-1), indicating that due to high soil pH (8.00), Pb may be precipitated as  $Pb(OH)_2$ . However, a high proportion ( $\sim 26$  %) of Pb is still in available form in this high-pH shooting range soil (Fig. 2a). Compared to the inorganic amendments, a greater SI value of chlorophyromorphite in the soils was observed with amendment of the BM, BC300, and BC700, due to the available  $PO_4^{3-}$ . The model predicted that Pb species in the BM-, BC300-, and BC700-amended soils were chloropyromorphite, hydroxylpyromorphite, and Pb(OH)2; however, no precipitations of PO<sub>4</sub><sup>3-</sup> species were found in the soils treated with the inorganic amendments (NRE, GINP, and AgNP), obviously due to lack of  $PO_4^{3-}$  in these amendments (Table 2).



**Fig. 2** Exchangeable (NH<sub>4</sub>OAc-extractable) (**a**) Pb, (**b**) Cu, and (**c**) Sb in the contaminated shooting range soil amended with natural iron oxide (NRE), gibbsite nanoparticle (GINP), silver nanoparticle (AgNP), biomass (BM), and its biochars produced at 300 (BC300) and 700 °C (BC700). *Error bars* represent the standard deviation of three replicates. The *same letters* above *each bar* indicate no difference at a 0.05 significance level

Changes in SI values were also observed for Cu species. Brochantite  $(Cu_4(SO)_4(OH)_6)$ , Cu-hydroxide  $(Cu(OH)_2)$ , langite  $(Cu_4(SO_4)(OH)_6.2H_2O)$ , and tenorite (CuO) minerals were predicted for all applied



Fig. 3 Toxicity characteristic leaching procedure (TCLP)— (a) Pb, (b) Cu, and (c) Sb in the contaminated shooting range soil amended with natural iron oxide (NRE), gibbsite nanoparticle (GINP), silver nanoparticle (AgNP), biomass (BM), and its biochars produced at 300 (BC300) and 700 °C (BC700). *Error* bars represent the standard deviation of three replicates. The same letters above each bar indicate no difference at a 0.05 significance level

amendments. Tsumebite  $(Pb_2Cu(PO_4)(SO_4)(OH))$  was predicted by the model in the soils amended with BM, BC300, and BC 700, which is a stable form of Cu





Fig. 4 Correlations between (a) pH and toxicity characteristic leaching procedure (TCLP)-Pb, (b) pH and TCLP-Cu, (c) cation exchange capacity (CEC) and TCLP-Pb, and (d) CEC and TCLP-Cu in the contaminated shooting range soil amended with

mineral (Frost and Palmer 2011). These models predicted transformations of metal species to more stable (less soluble) species in amendment-applied soils (Ahmad et al. 2014a). This is in agreement with the decreases in the extractability and leachability of Pb and Cu.

The association of Pb with other elements present in the soil system was investigated by elemental dot mapping, by selecting both soil and amendment particles. In the soils amended with BM, BC300, and BC700, Pb and P distributions were associated with each other, thus implying the formation of Pbphosphate species in organic amendment-applied soils (Fig. S2). In the control soil, the LCF analysis of the Pb<sub>L</sub>(III) EXAFS spectra identified that Pb was primarily associated with Pb-gibbsite (56.3 %) or hydrocerussite (7.6 %) (Table 3), including the

natural iron oxide (NRE), gibbsite nanoparticle (GINP), silver nanoparticle (AgNP), biomass (BM), and its biochars produced at 300 (BC300) and 700 °C (BC700)

adsorption of Pb into Al-containing minerals. Hydrocerussite is considered as a common Pb species present in a shooting range soil (Cao et al. 2003). Compared to the control soil, the amended soils showed clear difference in EXAFS spectra, indicating that the Pb species were transformed by the amendments (Fig. S3). Formation of Pb-oxide in the soils amended with NRE, GINP, and AgNP was observed, indicating Pb sorption by oxide forms of Al, Fe, or Ag. In the presence of moisture, the negatively charged metal nanoparticles form an outer metal oxide/hydroxide layer that facilitates the sorption/complexation of cationic Pb (Algudami et al. 2012). The additions of BM, BC300, and BC700 resulted in an increase in hydrocerussite (from 7.6 to 42.9, 20.2, and 10.3 %, respectively) components. Chloropyromorphite, a highly stable form of Pb, was observed in the

Mineral	$K_{\rm sp}$	Chemical formula	Saturation index (SI)								
			Control	NRE	GINP	AgNP	BM	BC300	BC700		
Pb											
Chloropyromorphite	$10^{-84.4}$	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	-15.53	-13.89	-15.04	-14.04	16.47	21.49	17.52		
Hydroxylpyromorphite	$10^{-62.8}$	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH	-20.25	-17.94	-19.20	-18.29	10.90	16.49	13.34		
Pb(OH) <sub>2</sub>	$10^{-17.09}$	Pb(OH) <sub>2</sub>	2.50	3.10	2.77	2.87	2.30	3.64	4.20		
Pb <sub>2</sub> (OH) <sub>3</sub> Cl	$10^{-8.79}$	Pb <sub>2</sub> (OH) <sub>3</sub> Cl	-0.39	0.15	-0.41	-0.10	0.08	2.18	2.48		
$Pb_3(PO_4)_2$	$10^{-43.5}$	$Pb_3(PO_4)_2$	-15.38	-14.04	-14.77	-14.20	5.45	-2.61	2.29		
$Pb_3O_2SO_4$	$10^{-10.69}$	$Pb_3O_2SO_4$	-0.48	0.10	-0.69	-0.23	-0.47	8.73	6.48		
Pb <sub>4</sub> (OH) <sub>6</sub> SO <sub>4</sub>	$10^{-21.1}$	Pb <sub>4</sub> (OH) <sub>6</sub> SO <sub>4</sub>	-0.24	0.93	-0.19	0.39	-0.43	3.44	1.79		
Pb <sub>4</sub> O <sub>3</sub> SO <sub>4</sub>	$10^{-21.88}$	Pb <sub>4</sub> O <sub>3</sub> SO <sub>4</sub>	-1.02	0.16	-0.97	-0.39	-1.20	2.66	2.95		
Cu											
Antlerite	$10^{8.8}$	Cu <sub>3</sub> (SO <sub>4</sub> )(OH) <sub>4</sub>	0.06	-0.61	-0.27	0.06	1.37	1.74	0.06		
Atacamite	$10^{7.39}$	Cu <sub>2</sub> Cl(OH) <sub>3</sub>	0.11	-0.18	0.01	0.22	1.44	2.10	1.46		
Brochantite	$10^{15.2}$	Cu <sub>4</sub> (SO <sub>4</sub> )(OH) <sub>6</sub>	3.82	3.35	3.71	4.11	5.37	6.36	4.77		
Cu(OH) <sub>2</sub>	$10^{13.7}$	Cu(OH) <sub>2</sub>	0.91	1.09	1.13	1.20	1.14	1.76	1.85		
Langite	$10^{17.5}$	Cu4(SO4)(OH)6.2H2O	1.55	1.08	1.45	1.85	3.11	4.09	2.50		
Tenorite	$10^{7.6}$	CuO	1.71	1.89	1.93	2.00	1.94	2.56	2.65		
Tsumebite	$10^{-9.79}$	$Pb_2Cu(PO_4)(SO_4)(OH)$	-4.14	-2.98	-3.48	-3.08	6.41	9.34	8.56		

**Table 2** Possible precipitation of metal minerals in thecontaminated shooting range soil amended with natural ironoxide (NRE), gibbsite nanoparticle (GINP), silver nanoparticle

(AgNP), biomass (BM), and its biochars produced at 300 (BC300) and 700  $^\circ$ C (BC700), as predicted by visual MINTEQ in an aqueous system

**Table 3** Relative proportions of Pb species in the contaminated shooting range soil amended with natural iron oxide (NRE), gibbsite nanoparticle (GINP), silver nanoparticle (AgNP),

biomass (BM), and its biochars produced at 300 (BC300) and 700  $^{\circ}$ C (BC700), determined by linear combination fittings (LCFs) on EXAFS spectra

0.261
0.267
0.213
0.201
0.147
0.182
0.152

<sup>a</sup> Normalized sum of the squared residuals of the fit

BM-, BC300-, and BC700-amended soils (20.5, 7.4, and 7.1 %, respectively), presumably indicating the decrease in availability and leachability of Pb. The formation of chloropyromorphite was favored in these soils because of highly available  $PO_4^{3-}$  contents originating from the BM and BCs. These observations are in agreement with SEM-elemental dot mapping data and thermodynamic modeling data.

Comparatively, the BCs outperformed nanomaterials (GINP and AgNP) and natural iron oxides (NRE) in remediating the metal-contaminated shooting range soil. This suggested that pure inorganic materials were less effective than organically and inorganically mixed materials such as BCs. Multiple mechanisms provoked by the complex nature of BC may have resulted in high metal immobilization efficiency. Another implication is that BCs induced greater changes in soil properties than nanomaterials, thereby significantly altering the metal species from available to more stable forms. However, none of the amendments was effective in decreasing the availability and leachability of Sb. Future research is needed to apply a suitable BC that can simultaneously immobilize metals and metalloids in co-contaminated soils such as shooting ranges. This can be further achieved by engineering the BC with physical or chemical modifications.

## Conclusion

The current study demonstrated that all soil amendments (buffalo weed biomass and its biochars produced at 300 and 700 °C, natural iron oxides, gibbsite, and silver nanoparticles) decreased the concentrations of NH<sub>4</sub>OAc-extractable Pb and Cu in the soils, whereas none of the amendments were suitable for Sb immobilization. Among the amendments examined, the biochar produced at 300 °C was the most effective for Pb and Cu immobilization in shooting range soils. Geochemical modeling and spectroscopic investigations revealed the formation of stable metal species in biochar-amended soils. In addition to the effectiveness for heavy metal immobilization, biochar application brings the additional benefit of soil quality improvements, such as CEC, SOC, and P in soil. Based on this result, we recommend field application together with colloidal movement of metals for further verification of the benefits of biochar application in the real environment.

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