J Soils Sediments (2017) 17:717–730
DOI 10.1007/s11368-015-1339-4

BIOCHAR FOR A SUSTAINABLE ENVIRONMENT

Biochar-induced changes in soil properties affected immobilization/mobilization of metals/metalloids in contaminated soils

Mahtab Ahmad[1,2] · **Sang Soo Lee**[1] · **Sung Eun Lee**[3] · **Mohammad I. Al-Wabel**[2] · **Daniel C. W. Tsang**[4] · **Yong Sik Ok**[1]

Received: 17 May 2015 / Accepted: 12 December 2015 / Published online: 25 January 2016

Abstract

Purpose Remediation of metal contaminated soil with biochar is attracting extensive interest in recent years. Understanding the significance of variable biochar properties and soil types helps elucidating the meticulous roles of biochar in immobilizing/mobilizing metals/metalloids in contaminated soils.

Materials and methods Six biochars were produced from widely available agricultural wastes (i.e., soybean stover, peanut shells and pine needles) at two pyrolysis temperatures of 300 and 700 °C, respectively. The Pb-, Cu-, and Sb-contaminated shooting range soils and Pb-, Zn-, and As-contaminated agricultural soils were amended with the produced biochars. The mobility of metals/metalloids was assessed by the standard batch leaching test, principal component analysis and speciation modeling.

Results and discussion The changes in soil properties were correlated to feedstock types and pyrolysis temperatures of biochars based on the principal component analysis. Biochars produced at 300 °C were more efficient in decreasing Pb and Cu mobility (>93 %) in alkaline shooting range soil via surface complexation with carboxyl groups and Fe-/Al-minerals of biochars as well as metal-phosphates precipitation. By contrast, biochars produced at 700 °C outperformed their counterparts in decreasing Pb and Zn mobility (100 %) in acidic agricultural soil by metal-hydroxides precipitation due to biochar-induced pH increase. However, Sb and As mobility in both soils was unfavorably increased by biochar amendment, possibly due to the enhanced electrostatic repulsion and competition with phosphate.

Conclusions It is noteworthy that the application of biochars is not equally effective in immobilizing metals or mobilizing metalloids in different soils. We should apply biochar to multi-metal contaminated soil with great caution and tailor biochar production for achieving desired outcome and avoiding adverse impact on soil ecosystem.

Keywords Bioavailability · Black carbon · Charcoal · Plant biomass · Soil contamination · Soil remediation

1 Introduction

In the last few years, biochar has been extensively used as a green environmental material for the remediation of contaminated soil and purification of water/wastewater (Ahmad et al. 2014a; Mohan et al. 2014; Tsang and Yip 2014; Rinklebe and Shaheen 2015). Biochar is a solid product obtained from the thermochemical treatment of biomass under a limited oxygen environment (IBI 2012). Since the ancient production by slash-and-char technique, pyrolysis of biomass is now widely

---

Responsible editor: Jianming Xu

Electronic supplementary material The online version of this article (doi:10.1007/s11368-015-1339-4) contains supplementary material, which is available to authorized users.

✉ Daniel C. W. Tsang
dan.tsang@polyu.edu.hk

✉ Yong Sik Ok
soilok@kangwon.ac.kr

[1] Korea Biochar Research Center, Kangwon National University, Chuncheon 24341, Korea

[2] Soil Sciences Department, College of Food and Agricultural Sciences, King Saud University, P.O. Box 2460, Riyadh 11451, Kingdom of Saudi Arabia

[3] School of Applied Biosciences, Kyungpook National University, Daegu 41566, Korea

[4] Department of Civil and Environmental Engineering, Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

used to obtain biochar and bioenergy. Pyrolytic conditions such as temperature, heating rate, and residence time have been reported to significantly influence the characteristics of produced biochar, in addition to biomass type (Al-Wabel et al. 2013). Therefore, it is important to select suitable biomass and optimize pyrolysis conditions to obtain appropriate biochar. Generally, biomass including agricultural waste, wood waste, and fruit and vegetable waste, containing high lignin and cellulose, is subjected to a slow pyrolysis (heating rate of >5 °C min^{-1} at 200–800 °C for a residence time of >2 h) to produce high yield biochar (Ahmad et al. 2014a).

Soil is considered as a major sink of heavy metals and metalloids originating from anthropogenic activities (Wuana and Okieimen 2011), and subsequently become a long term contamination source. In particular, agricultural soils close to abandoned metal mines and open-field shooting range soils are highly contaminated with metals and metalloids (Ok et al. 2010; Ahmad et al. 2012a). These metals and metalloids co-contaminated soils are challenging for remediation because of contrasting fate and chemistry of metals and metalloids in soils (Clemente et al. 2008). Mobility of cationic metals and anionic metalloids in soils is affected by soil amendments in a different ways. Complexation is an important mechanism controlling mobility of cationic metals, whereas competition for available sites on soil minerals between metalloids and soil amendments could be a dominant factor involved in sorption/desorption of metalloids (Violante et al. 2010). Several organic and inorganic soil amendments are described to reduce the mobility and bioavailability of metals/metalloids in contaminated soils (Ahmad et al. 2012b; Tsang et al. 2014). However, depending on the environmental conditions, increased mobilization of metalloids in these co-contaminated soils has often been observed when treated with soil amendments (Uchimiya et al. 2012; Lim et al. 2013; Tsang et al. 2013). Therefore, careful examination is needed in selecting an appropriate soil amendment for the remediation of metal/metaloid-contaminated soils. A combination of amendments is also suggested for immobilizing both metals and metalloids in soil (Mench et al. 2007; Tsang et al. 2013).

In the past few years, biochars originating from various feedstocks have been tested for remediation of metals/metalloids contaminated soils (Beesley et al. 2013; Herath et al. 2015; Rajapaksha et al. 2015). Most of the studies focused on cationic metals such as Cd, Cu, Pb, Ni, and Zn while fewer on anionic metalloids such as As and Sb and their simultaneous contamination with metals (Beesley et al. 2010; Ahmad et al. 2014a; Tsang et al. 2014). The mobility and bioavailability of As in soils have received greater attention worldwide compared to those of Sb, which could be related to the severe health impacts of As that is naturally present in many geological regions. On the contrary, Sb contamination in soil is generally localized and associated with Cu and Pb smelters as well as shooting ranges (Violante et al. 2010; Ahmad et al. 2014b). There is insufficient understanding about the correlation between various types of biochar having different characteristics and their remediation efficacy for metal- and metalloid-contaminated soils. Although biochar demonstrates a greater stability in a soil compared to other organic amendments such as compost and hydrochar (Busch and Glaser 2015), the ionic properties of biochar and its release of cations and anions may strongly alter the mobility of metals/metalloids (Uchimiya et al. 2011).

In this study, six biochars were produced from different feedstocks at two different pyrolysis temperatures, which were testified for the immobilization/mobilization of metals and metalloids in two different contaminated soils. The significance of ionic properties of biochar on soil properties and mobility of metals/metalloids was assessed by means of batch leaching, principal component analysis, and speciation modeling.

2 Materials and methods

2.1 Soils collection and characterization

The soils were collected from an active military shooting range and an agricultural land in Gangwon-do, Korea, respectively. Shooting range soil was collected from Cheorwon-gun while an agricultural soil was collected from an agricultural land adjacent to the closed Poong-Jeong mine. The soil samples were air-dried, sieved through a 2-mm aperture and subjected to selected physico-chemical analyses including soil texture, pH, electrical conductivity (EC), exchangeable cations (Ca, Mg, Na, and K), cation exchangeable capacity (CEC), and total metal/metalloid (Pb, Cu, Zn, As, and Sb) content. Standard test procedures were adopted to characterize soils for basic parameters (Sparks et al. 1996). Total metal/metalloid contents were determined by acid digestion of the soils in a microwave assisted digestion unit (MARS, HP-500 plus, CEM Corp., USA) following the USEPA method 3051A by an inductively coupled plasma optical emission (ICP-OES) spectrometer (Optima 7300 DV, Perkin Elmer, USA).

2.2 Biochars production and characterization

Different feedstocks including soybean stover (SS), peanut shells (PS) and pine needles (PN) were converted to biochars via thermal pyrolysis. The feedstock materials were first air-dried in an oven at 60 °C, grinded, and sieved through a 1-mm aperture to get homogeneous particle size. The powdered materials were placed in covered ceramic crucibles, and pyrolyzed in a muffle furnace (MF 21GS, Jeio Tech, Korea) under limited supply of air at a slow pyrolysis rate of 7 °C min^{-1}. Two different peak temperatures, i.e., 300 and 700 °C, were employed and held for 3 h. The produced biochar (BC) was

Table 1 Selected physicochemical properties of soils

	Sand	Silt	Clay	pH[a]	EC[b]	Exchangeable cations				CEC[c]	Total metals[d]						
						Ca	Mg	Na	K		Pb	Cu	Zn	As	Sb	Fe	Al
	%				dS m^{-1}	cmol kg^{-1}				cmol kg^{-1}	mg kg^{-1}						
Shooting range soil	67.1	26.9	6.0	8.0	0.05	1.19	1.27	0.05	0.21	2.72	17468	1168	165	BDL	164	16010	16774
Agricultural soil	83.4	8.6	8.0	5.8	0.03	7.32	1.58	0.03	0.19	16.2	1945	71.5	448	171	ND	18331	34466
Warning level	–	–	–	–	–	–	–	–	–	–	200	150	300	25	5	–	–

BDL below detection limit, *ND* not determined

[a] 1:5 soil/water ratio

[b] Electrical conductivity at 1:5 soil/water ratio

[c] Cation exchangeable capacity

[d] Aqua regia extracted

allowed to cool inside the furnace and then stored in airtight containers. In this way, six BCs, namely SS-BC300, SS-BC700, PS-BC300, PS-BC700, PN-BC300, and PN-BC700 were obtained, where the prefix and suffix represent the feedstock type and pyrolysis temperature, respectively. Proximate analysis of BCs was conducted for mobile/volatile matter, residual matter, and ash contents following the methods described by Ahmad et al. (2012a). Chemical and ultimate analyses were also performed to determine pH, EC, CEC, and elemental composition (C, H, N, and O) of BCs. An elemental analyzer (EA1110, CE Instruments, Italy) was used for measuring elemental composition of BCs. The specific surface area of BCs was determined by a gas sorption analyzer (NOVA-1200, Quantachrome Corp., USA).

2.3 Batch leaching experiment

Standard batch leaching test, described in DIN 38414 S4 guidelines, for contaminants release from soils was employed to examine the role of different BCs in controlling the mobility of metals/metalloids (Al-Tabbaa and Perera 2006; Ahmad et al. 2012d). According to the above guideline, 10 g of each soil was thoroughly homogenized with or without 10 wt% of different BCs in a glass reactor. Deionized water (aquaMAX, 18.2 MΩ cm resistivity) was added at a liquid/solid ratio of 10:1. The mixtures were equilibrated on a mechanical shaker for 24 h, followed by filtration through a 0.45-μm Whatman filter paper. The filtered soil solutions were then analyzed for pH, EC, anions (Cl, NO_3, PO_4, and SO_4), cations (Na, K, Ca, Mg, Fe, and Al), and dissolved organic carbon. Anions were measured on an ion chromatograph (Metrohm Compact IC-861, Switzerland) while cations and released metals/metalloids (Pb, Cu, Zn, As, and Sb) in the soil solution were analyzed by an ICP-OES. The water soluble metals/metalloids contents of the two soils are shown in Table S1 of the Electronic Supplementary Material. Dissolved organic carbon was measured by a total organic carbon analyzer (TOC-ASI, Shimadzu, Japan).

Solid phase metal availability was assessed using the thermodynamic speciation model Visual MINTEQ (ver. 3.0). The model is widely used to predict possible precipitation of metal minerals that control their solubilities in soil solution (Hashimoto et al. 2009). The ionic concentrations and dissolved organic carbon were used as model input parameters, with 25 °C and CO_2 pressure of $10^{-3.4}$ atm at fixed aqueous pH values. The model database of equilibrium constants and

Table 2 Proximate and ultimate analysis of different types of biochar

Sample	Mobile matter %	Residual matter %	Ash %	pH[a] –	EC[b] dS m^{-1}	CEC[c] $cmol_{(+)}$ kg^{-1}	C %	H %	N %	O %	Surface area m^2 g^{-1}
SS-BC300	46.3	38.8	10.4	7.9	0.55	110	68.8	4.29	1.86	25.0	5.61
SS-BC700	14.7	67.7	17.2	10.4	0.83	144	82.0	1.27	1.29	15.5	420
PS-BC300	60.5	37.0	1.24	7.6	0.15	33.2	68.3	3.85	1.91	25.9	3.14
PS-BC700	32.7	58.1	8.91	9.7	0.32	74.3	83.8	1.75	1.14	13.3	448
PN-BC300	38.6	54.2	7.20	7.2	0.07	6.60	84.2	4.37	3.88	7.57	4.09
PN-BC700	6.20	75.0	18.7	9.7	0.29	52.0	93.7	0.62	3.64	2.07	391

[a] 1:10 biochar/water ratio

[b] Electrical conductivity at 1:10 biochar/water ratio

[c] Cation exchangeable capacity

thermodynamic reactions was applied to provide theoretical prediction of the minerals in two soils. Saturation index (SI) values of >0 were assumed to present supersaturation of the solution with respect to minerals. The SI was calculated using the following equation (Hashimoto et al. 2009):

$$SI = \log IAP - \log K_{sp}$$

where IAP and K_{sp} are the ion activity product and solubility product, respectively.

2.4 Statistical and principal component analyses

The results were expressed as averaged values of three replicates with standard deviations. Correlation coefficient (R^2) values were calculated from linear regressions between various soil and BC properties. Statistical analyses were conducted using the SAS package (version 9.2, SAS Institute, Cary, NC, USA). One way ANOVA and Tukey's honest significant difference (HSD) studentized range tests were applied to differentiate between various treatments at a 0.05 significance level. Multivariate approach of principal component analysis (PCA) was employed to determine chemical fingerprints and contribution of each fingerprint to source. The Xlstat (Addinsoft USA, New York, NY) software was used for PCA.

3 Results and discussion

3.1 Soils characteristics

The properties of shooting range and agricultural soils are presented in Table 1. Shooting range soil was sandy loam (67.1 % sand, 26.9 % silt and 6.0 % clay) and alkaline (pH 8.0) with low CEC (2.72 cmol kg^{-1}). It was highly contaminated with Pb (17,468 mg kg^{-1}), Cu (1,168 mg kg^{-1}), and Sb (164 mg kg^{-1}); which represented 87 times higher than the Pb warning level of 200 mg kg^{-1}, 7.8 times higher than the Cu warning level of 150 mg kg^{-1}, and 33 times higher than the Sb warning level of 5 mg kg^{-1}, respectively, in Korea (Olive 2006; MOE 2010). The contamination of a military shooting range soil with metals and metalloids has been commonly reported as a result of weathering of spent bullets (Cao et al. 2003; Ahmad et al. 2014b). On the other hand, agricultural soil was loamy sand (83.4 % sand, 8.6 % silt and 8.0 % clay) and acidic (pH 5.8) with normal CEC (16.2 cmol kg^{-1}). It was contaminated with Pb (1,945 mg kg^{-1}), Zn (448 mg kg^{-1}) and As (171 mg kg^{-1}); similarly representing 9.7 times higher than the Pb warning level of 200 mg kg^{-1}, 1.5 times higher than the Zn warning level of 300 mg kg^{-1}, and 6.8 times higher than the As warning level of 25 mg kg^{-1}, respectively (MOE 2010). Such contamination of agricultural soil was attributed to the transportation of metals/metalloids from a nearby abandoned metal mine (Lim et al. 2013).

3.2 Biochar characteristics

The results of proximate and ultimate analyses of different BCs are presented in Table 2. High pyrolysis temperature (700 °C) resulted in low content of mobile matter and high contents of ash and residual matter due to greater loss of volatile matter from the feedstock as compared to pyrolysis at 300 °C. Among different feedstocks, PS showed a higher stability against loss of mobile matter (6.48 %) compared to SS (14.7 %) and PN (22.6 %). This could be attributed to high lignin content in PS (Fang et al. 2014); because lignin decomposes slowly with increasing temperature than cellulose resulting in high char yield (Giudicianni et al. 2013; Brebu

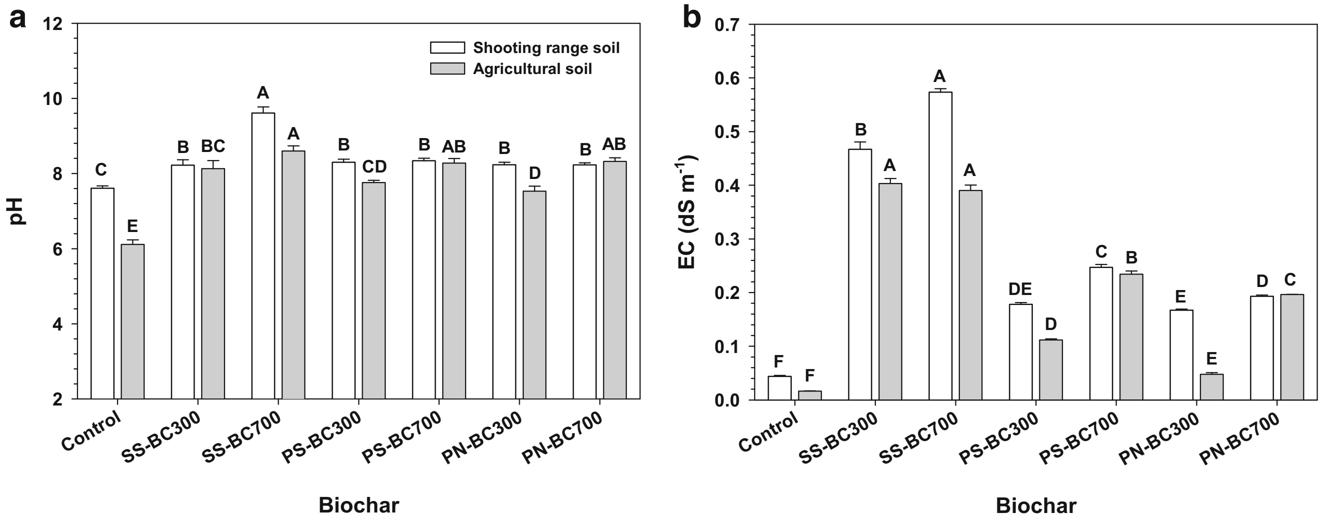
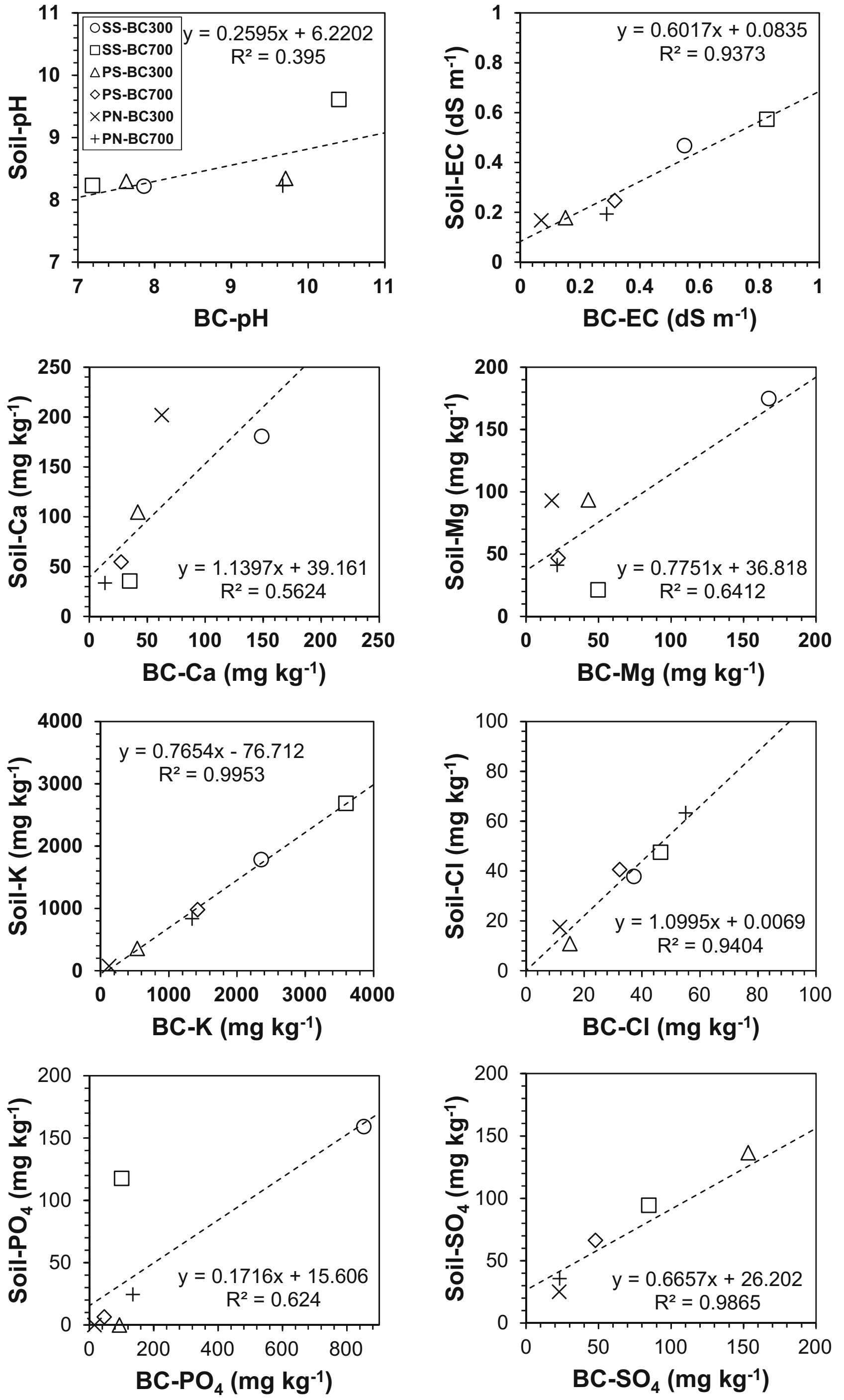


Fig. 1 Changes in **a** pH and **b** EC of shooting range and agricultural soils treated with different types of biochars (*bars with different letters above* are significantly different at $P < 0.05$)

and Vasile 2010). High ash contents were observed for BCs pyrolyzed at 700 °C indicating accumulation of inorganic minerals, which could raise pH, EC, and CEC. These results are in agreement with previously reported studies (Al-Wabel et al. 2013; Zhang et al. 2015). Based on ash and moisture free basis, the C contents were also high for BCs produced at 700 °C due to high carbonization at high temperature (Ahmad et al. 2012c). The PN pyrolyzed at 700 °C exhibited the maximum C content (93.7 %). Other elements (H, O and N) were decreased with increasing pyrolysis temperature from 300 °C to 700 °C, reflecting a loss of functional groups with volatile matter at high temperature. Surface area of BCs produced at 700 °C was enormously high (ranging from 391 to 448 m^2 g^{-1}) compared to BCs produced at 300 °C (ranging from 3.14 to 5.61 m^2 g^{-1}). This could be ascribed to the development of micropores and mesopores resulting from evolution of gases at high pyrolysis temperature (Klasson et al. 2014). As pyrolysis temperature and feedstock type showed

Fig. 2 Correlations between ionic properties of biochars and shooting range soil



prominent effects on BC properties, the effects of BCs were likely to be variable on soil properties and metals/metalloids immobilization/mobilization.

3.3 Changes in soil properties due to biochar amendment

The BC addition significantly affected soil pH and EC as shown in Fig. 1. All BCs increased pH of both shooting range and agricultural soils. The maximum increase in pH was observed in soils treated with SS-BC700, causing an increase of 2 and 2.5 units in alkaline shooting range and acidic agricultural soils, respectively, compared to the control. This could be attributed to buffering capacity of two different soils, where sandy loam alkaline soils generally possess a higher buffering capacity than loamy sand acidic soils (Merry 2010). Soil EC was also significantly increased by all types of BCs. In particular, SS-BCs tremendously increased EC to a maximum of 0.57 and 0.40 dS m^{-1} in shooting range and agricultural soils, respectively. The regression coefficients were calculated from linear relationships between various parameters of BCs and soils, as shown in Figs. 2 and 3. Both pH and EC of soils were positively correlated with those of BCs, respectively. In addition, increases in soil cations (Ca, Mg, and K) and anions (Cl, PO_4, and SO_4) were directly related to the ionic contents of BCs.

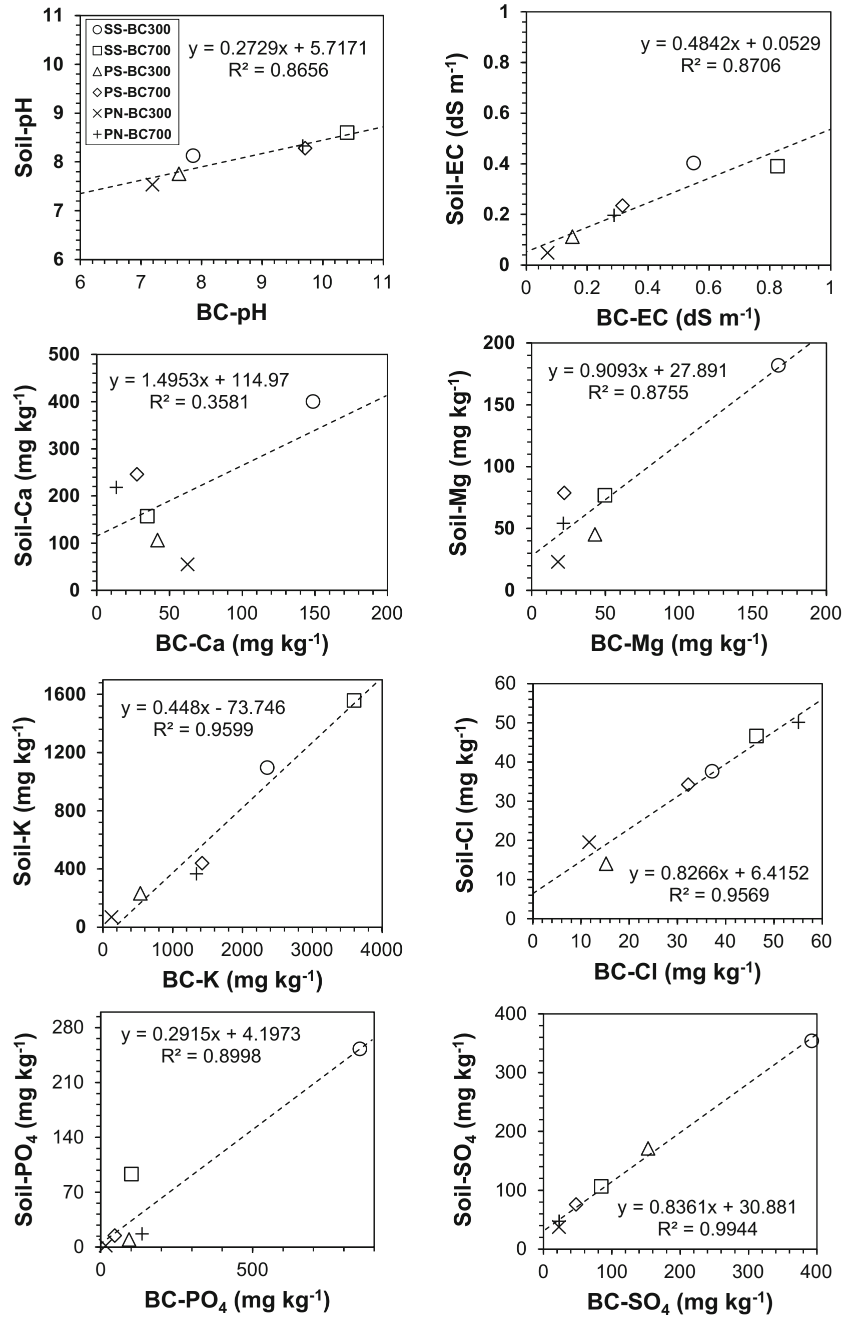


Fig. 3 Correlations between ionic properties of biochars and agricultural soil

It is noteworthy that BCs were not equally effective in increasing the ionic properties of amended soils. For example, in shooting range soil (Fig. 2), BCs produced at 300 °C resulted in higher Ca, Mg, and SO_4 contents while BCs produced at 700 °C led to higher K, Cl and PO_4 contents. However, in agricultural soil (Fig. 3), all cationic and anionic contents except SO_4 were higher with amendment of BCs produced at 700 °C. Among different BCs, SS-BCs and PN-BCs resulted in the maximum increase in ionic concentrations of amended soils. It was evident that ions were mostly released from the BC itself rather than the soil. The high release of cations and anions from BCs, especially those produced at 700 °C, could be related to the presence of soluble salts (as seen in high EC values in Table 2), since they were not subjected to washing after pyrolysis. Therefore, BCs can serve to replenish and retain exchangeable nutrient ions such as Ca, Mg, NO_3, and PO_4 in the amended soils (Yao et al. 2012).

3.4 Dissolved carbon in soil-biochar systems

Dissolved total, inorganic and organic C contents in BC treated shooting range and agricultural soils are shown in Fig. 4. Compared to the control, SS-BC300 was most effective in increasing dissolved C contents in both shooting range and agricultural soils. The release of dissolved C into soil solution of amended soils was linearly correlated ($R^2 = 0.989$ for

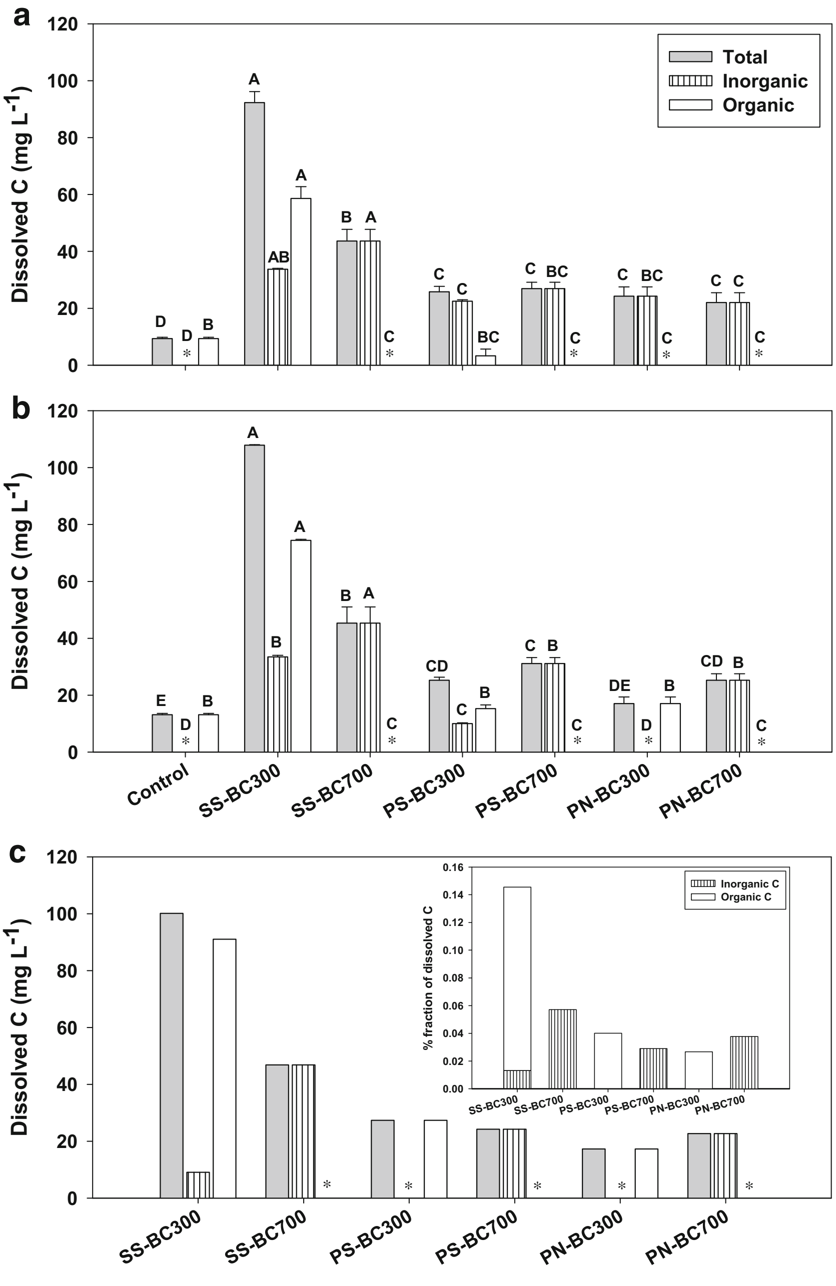


Fig. 4 Dissolved carbon (C) contents in biochar treated **a** shooting range soil, **b** agricultural soil, and **c** different types of biochars by themselves (*bars with different letters above* are significantly different at $P < 0.05$; * indicates concentrations below detection limit)

shooting range soil and $R^2 = 0.988$ for agricultural soil) with dissolved C of BCs, indicating that BC was the source of C release. Dissolved organic C contents in BCs produced at 700 °C were negligible owing to the loss of mobile organic matter (Table 2) during pyrolysis at this temperature. In other words, increasing pyrolysis temperature enhanced recalcitrance of BC and rendered C more stable in soils, as shown in previous studies (Ahmad et al. 2014a; Crombie and Masek 2015). Moreover, dissolved organic C in original soils was made immobile by all types of BC700 and became negligible in soil solutions (Fig. 4a,b), possibly indicating sorption and retention of readily soluble organic matter in the soils (Cabrera et al. 2014). Interestingly, dissolved inorganic C fraction was dominant in BCs produced at 700 °C (inset in Fig. 4c). This suggested the presence of carbonates in the form of calcite and/or dolomite in these BCs (Yuan et al. 2011). As a result, the soils amended with all types of BC700 showed a notable increase in dissolved inorganic C contents compared to those amended with respective BC300 (Fig. 4a,b).

3.5 Principal component analysis of soil quality parameters

Three principal components were obtained from shooting range and agricultural soils by conducting multivariate PCA (Fig. 5). In the BCs treated shooting range soil (Fig. 5a), chemical fingerprints indicated that dissolved total C (12.5 %), SO_4 (10.7 %), PO_4 (10.6 %) and EC (10.5 %) mainly contributed to factor 1 (F1) while Ca (14.4 %), Cl (13.7 %), Mg (12.9 %), pH (12.8 %) and K (12.5 %) mainly contributed to factor 2 (F2), and dissolved organic C (20.1 %), Fe (17.6 %), Al (17.5 %) and pH (10.9 %) mainly contributed to factor 3 (F3), respectively. Among six different BCs, F1 highly contributed to SS-BC300 (48.7 %) followed by SS-BC700 (9.40 %) and PN-BC700 (7.92 %) while F1 contribution to other BCs was negligible (Fig. 5c). This indicated that SS-BC300, SS-BC700 and PN-BC700 were mainly responsible for increasing dissolved total C, SO_4, PO_4, and EC of the shooting range soil. The contributions of F2 to SS-BC700 (52.4 %), PN-BC300 (17.4 %) and PS-BC300 (13.3 %) emphasized their significance in increasing Ca, Cl, Mg, pH and K contents in the shooting range soil. Based on F3 contributions, SS-BC300 (28.3 %) and PN-BC300 (22.1 %) showed an influence on dissolved organic C, Fe and Al contents of the shooting range soil. Overall, PCA results indicated that SS-BC300 and SS-BC700 played a principal role in improving the chemical properties and ecological qualities of the shooting range soil, compared to other BCs.

In the BCs treated agricultural soil (Fig. 5b), chemical fingerprints indicated that EC (10.0 %), Mg (9.61 %), Ca (9.40 %) and dissolved total C (8.58 %) contributed to F1 (Fig. 5b) while dissolved organic C (24.7 %), SO_4 (12.5 %)

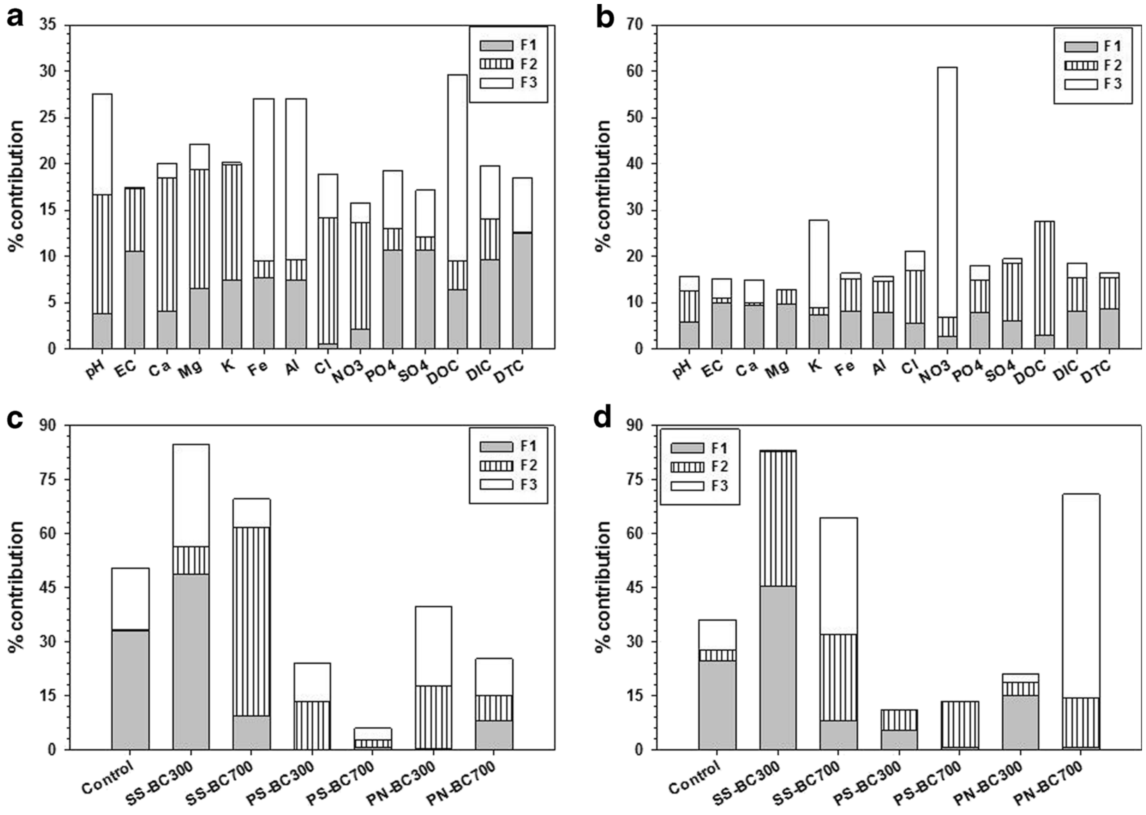


Fig. 5 Chemical fingerprints and contribution of principal component analysis (PCA) factors obtained from (**a**, **c**) shooting range soil and (**b**, **d**) agricultural soil treated with different types of biochars

and Cl (11.3 %) contributed to F2, and NO_3 (54.1 %) and K (18.8 %) contributed to F3. Among six different BCs, F1 highly contributed to SS-BC300 (45.3 %) followed by PN-BC300 (15.0 %) and SS-BC700 (8.10 %) while its contribution to other BCs was negligible (Fig. 5d). This indicated that SS-BC300, PN-BC300 and SS-BC700 were influential for EC, Mg, Ca and dissolved total C of the agricultural soil. Similarly, the contributions of F2 to SS-BC300 (37.7 %), SS-BC700 (23.9 %), PN-BC700 (13.6 %) and PS-BC700 (12.7 %) suggested that they increased the contents of dissolved organic C, SO_4 and Cl in the agricultural soil. Based on F3 contributions, PN-BC700 (56.6 %) and SS-BC700 (32.5 %) showed a remarkable influence on NO_3 and K contents. Overall, in the agricultural soil, SS-BC300 and PN-BC700 were most effective for enhancing the soil qualities. Thus, chemical fingerprints and contribution of PCA factors corroborated that different types of BCs are responsible for modifying different soil chemical properties, and their corresponding contributions also vary with soil types.

3.6 Immobilization/mobilization of metals/metalloids in biochar-amended soils

As shown in Fig. 6a, all BCs except PN-BC700 significantly decreased the mobility of Pb and Cu in the shooting range soil, where SS-BC300, PS-BC300, and PN-BC300 were equally

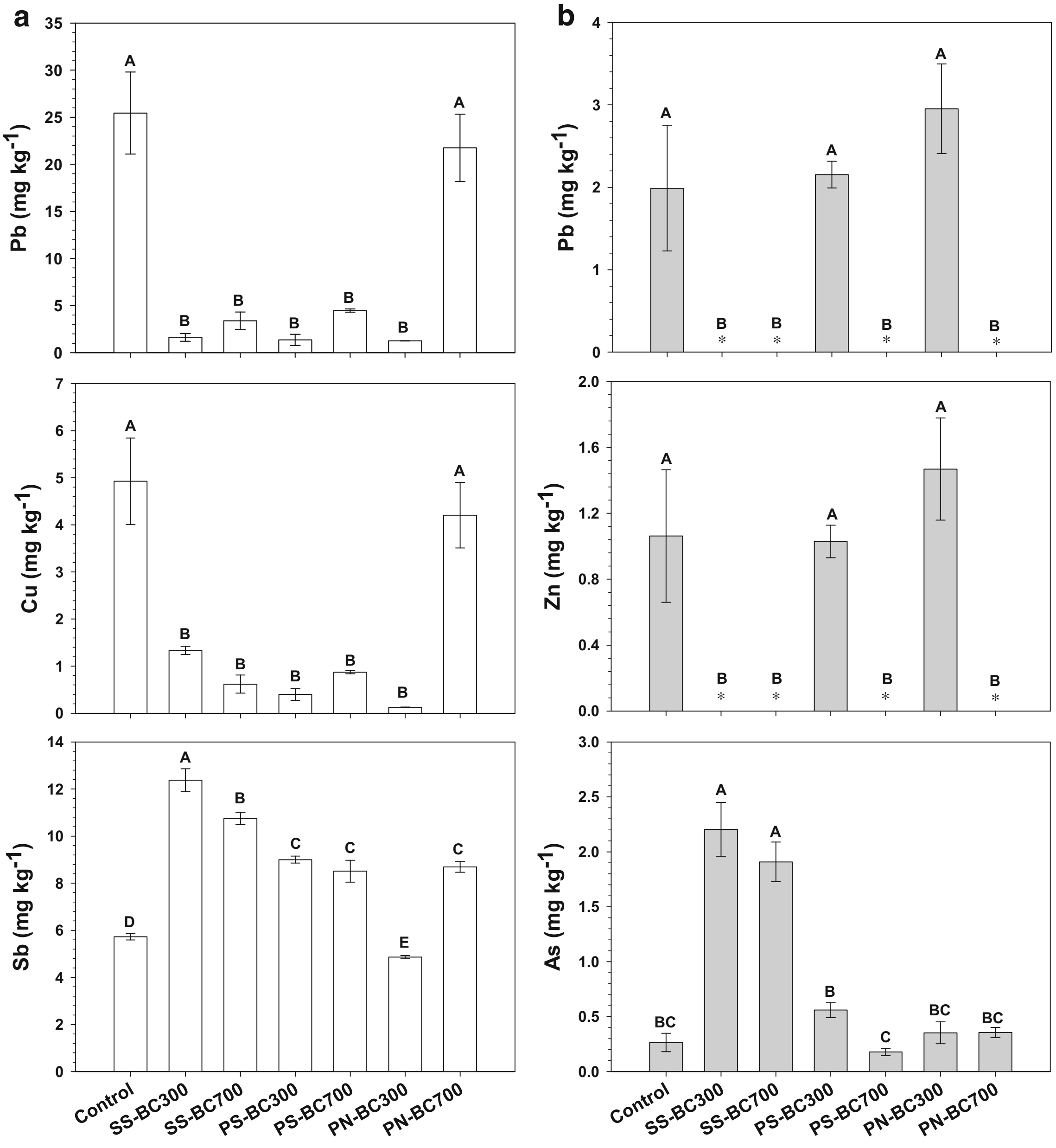


Fig. 6 Metals/metalloids mobility in **a** shooting range soil and **b** agricultural soil treated with different types of biochars (bars with different letters above are significantly different at $P < 0.05$; * indicates concentrations below detection limit)

Table 3 Mineral precipitation in shooting range and agricultural soils treated with different biochars based on Visual MINTEQ speciation modeling

Mineral	Chemical formula	K_{sp}	Control	SS-BC300	SS-BC700	PS-BC300	PS-BC700	PN-BC300	PN-BC700
Pb			Saturation index (shooting range soil)						
Chloropyromorphite	$Pb_5(PO_4)_3Cl$	$10^{-84.4}$	−15.4	12.7	17.6	18.0	18.9	17.9	20.5
Hydroxylpyromorphite	$Pb_5(PO_4)_3OH$	$10^{-62.8}$	−25.1	3.11	9.38	8.69	9.52	8.66	10.9
$Pb(OH)_2$	$Pb(OH)_2$	$10^{-17.09}$	0.605	−0.785	2.72	0.972	1.37	1.33	1.22
$Pb_3(PO_4)_2$	$Pb_3(PO_4)_2$	$10^{-43.5}$	−18.0	1.29	4.30	4.42	4.84	4.28	5.78
$PbHPO_4$	$PbHPO_4$	$10^{-23.8}$	−11.3	−0.997	−1.25	−0.311	−0.301	−0.561	0.246
Plumbogummite	$PbAl_3(PO_4)_2(OH)_5.H_2O$	$10^{-32.8}$	−9.85	10.3	2.21	9.79	9.28	9.15	11.0
Tsumebite	$Pb_2Cu(PO_4)(SO_4)(OH)$	$10^{-9.79}$	−7.37	−0.930	6.17	4.36	5.17	4.80	5.44
Cu									
Antlerite	$Cu_3(SO_4)(OH)_4$	$10^{8.8}$	−1.18	−8.65	−0.516	−0.593	0.093	−0.076	−0.256
Atacamite	$Cu_2Cl(OH)_3$	$10^{7.39}$	−0.893	−6.04	0.314	−0.645	0.298	0.043	0.333
Brochantite	$Cu_4(SO_4)(OH)_6$	$10^{15.2}$	1.61	−8.37	3.60	2.53	3.62	3.38	3.15
$Cu(OH)_2$	$Cu(OH)_2$	$10^{13.7}$	−0.063	−2.57	1.26	0.269	0.669	0.601	0.548
$Cu_3(PO_4)_2$	$Cu_3(PO_4)_2$	$10^{-36.8}$	−23.3	−7.33	−3.34	−0.947	−0.531	−1.17	0.502
Langite	$Cu_4(SO_4)(OH)_6.2H_2O$	$10^{17.5}$	−0.657	−10.6	1.34	0.266	1.35	1.12	0.881
Tenorite	CuO	$10^{7.6}$	1.59	−0.923	2.912	1.92	2.32	2.25	2.20
Tsumebite	$Pb_2Cu(PO_4)(SO_4)(OH)$	$10^{-9.79}$	−7.37	−0.930	6.17	4.36	5.17	4.80	5.44
Pb			Saturation index (agricultural soil)						
Chloropyromorphite	$Pb_5(PO_4)_3Cl$	$10^{-84.4}$	4.30	2.99	5.35	4.37	5.44	5.00	6.67
Plumbogummite	$PbAl_3(PO_4)_2(OH)_5.H_2O$	$10^{-32.8}$	12.4	8.81	5.47	9.98	6.94	13.1	7.69
Zn									
$Zn_3(PO_4)_2.4H_2O$	$Zn_3(PO_4)_2.4H_2O$	$10^{-35.4}$	−9.62	1.24	0.176	−0.548	−0.140	−2.20	0.690

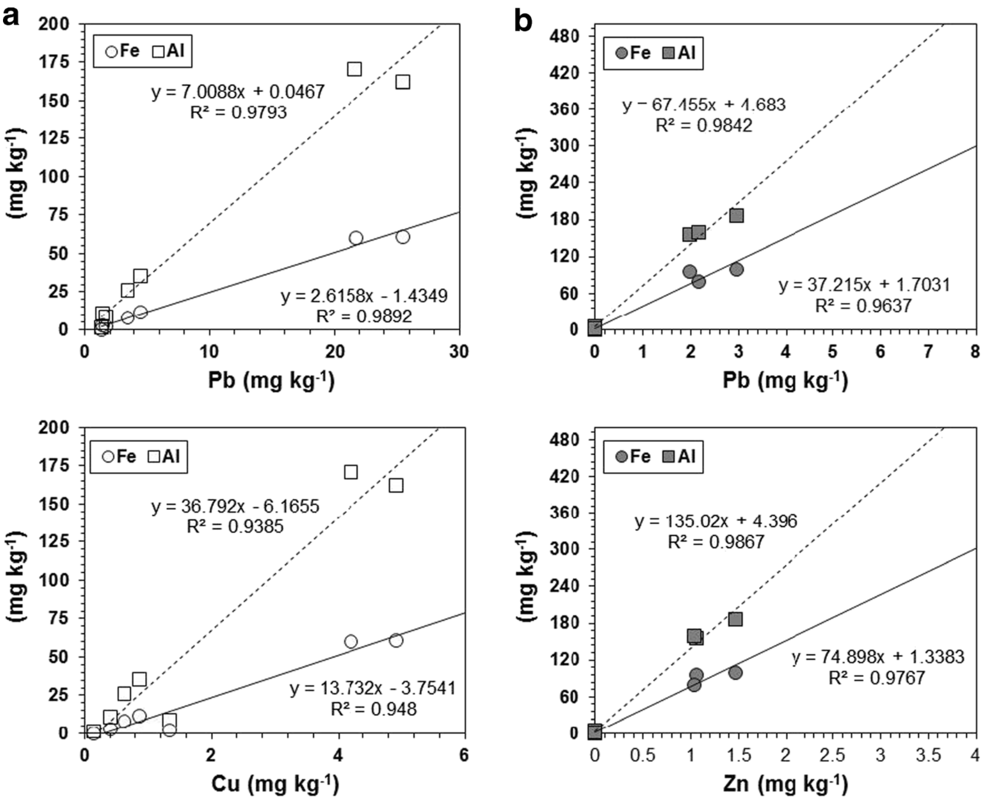


Fig. 7 Fe and Al concentrations as a function of Pb, Zn, and Cu concentrations in **a** shooting range soil and **b** agricultural soil treated with different types of biochars

effective in reducing Pb mobility by 94 % while PN-BC300 offered the maximum reduction of Cu mobility by 97.5 %. The high effectiveness of BCs produced at 300 °C towards Pb and Cu immobilization was attributed to greater O contents (Table 2), because divalent metals have shown greater affinity to form surface complexes with O-containing (e.g., carboxyl, −COOH) functional groups (Uchimiya et al. 2011; Tsang et al. 2013). On the other hand, anomalous behavior of PN-BC700 towards Pb and Cu mobility could also be explained by its low O and H contents (Table 2). On the contrary, all BCs except PN-BC300 significantly increased the mobility of Sb because of the opposite electrostatic charge of anionic metalloids. Organic amendments such as BCs and composts have been found to enhance the mobility of anionic metalloids due to electrostatic repulsion to negatively charged soil surfaces (Clemente et al. 2010; Beesley et al. 2013; Tsang and Yip 2014). The PN-BC300 showed a slight but significant decrease in Sb mobility (15.1 %). This may result from high affinity sorption of Sb onto amine functional group (Iqbal et al. 2013), which was possibly present in a larger amount in PN-BC300 in view of its high N content (3.88 %, Table 2). In addition, relatively small CEC (6.60 $\text{cmol}_{(+)}\ \text{kg}^{-1}$) of PN-BC300 may not induce electrostatic repulsion between soil particles and Sb.

In the agricultural soil (Fig. 6b), Pb and Zn were completely immobilized by SS-BC300, SS-BC700, PS-BC700 and PN-BC700, whereas other BCs did not show significant changes in Pb and Zn mobility. Such immobilization in the agricultural soil could be related to formation of Pb- and Zn-hydroxide precipitates under alkaline pH conditions (>8.0, Fig. 1), which was induced by all BCs produced at 700 °C possessing high pH values of 9.7-10.4 (Table 2). In contrast, ineffectiveness of PS-BC300 and PN-BC300 for Pb and Zn immobilization could be attributed to a relatively small increase in soil pH (<8.0, Fig. 1) as well as their low values of CEC (33.2 and 6.6 $\text{cmol}_{(+)}\ \text{kg}^{-1}$, respectively) compared to other BCs (Table 2). For an amended soil having a high CEC, more exchange sites are available for retaining the cationic metals (Silveria et al. 2003). Similar to Sb in the shooting range soil, As mobility was significantly increased in the

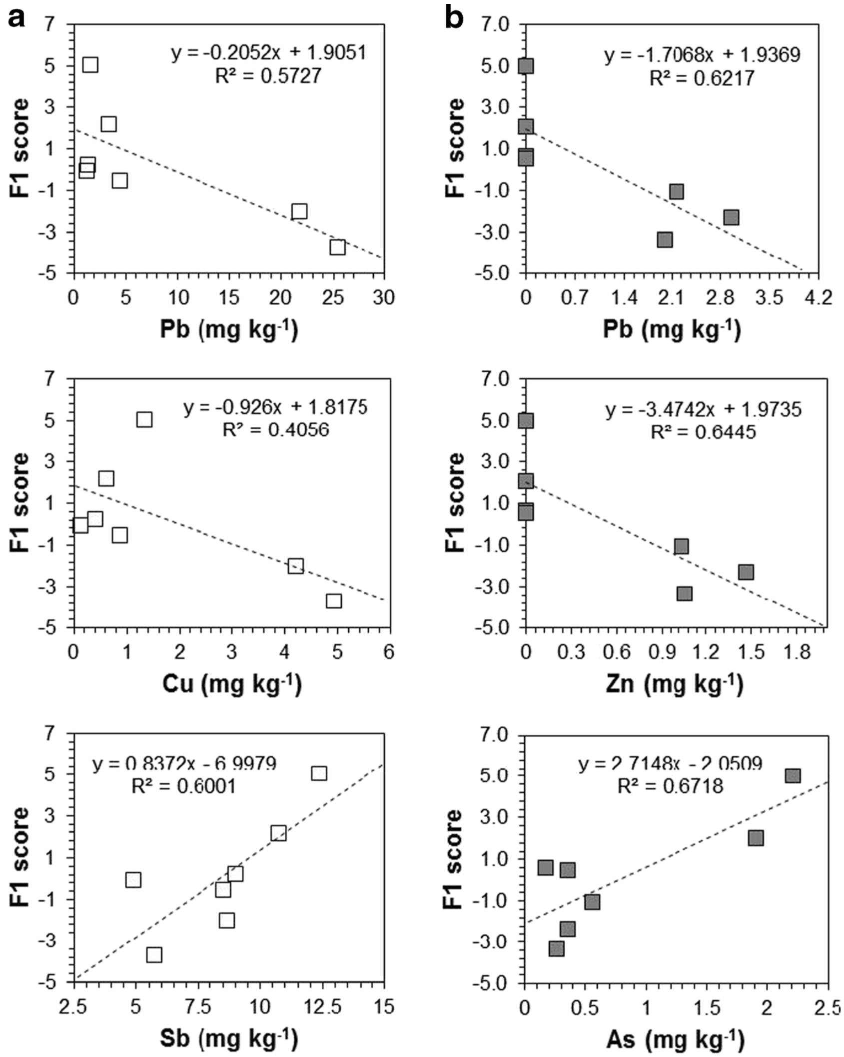


Fig. 8 Correlations between metals/metalloids concentrations and F1 scores of principal component analysis (PCA) for **a** shooting range soil and **b** agricultural soil treated with different types of biochars

agricultural soil amended with SS-BC300, SS-BC700 and PS-BC300. This was probably linked to high PO_4 contents in these BC amended agricultural soils (Fig. 3), as competition of sorption sites between PO_4 and As is well documented (Bolan et al. 2014).

These findings suggested that, in general, BCs immobilized metals (Pb, Zn, and Cu) but mobilized metalloids (As and Sb). However, the resultant mobility of metals and metalloids also depends on types and properties of both BCs and soils. In the BC treated shooting range soil solutions, geochemical modeling by the Visual MINTEQ predicted possible formation of stable Pb- and Cu-phosphate minerals including chloropyromorphite, hydroxylpyromorphite, plumbogummite, and tsumebite (Table 3). This was aligned with recent spectroscopic evidence of transformation of available Pb species in a shooting range soil to highly stable Pb-phosphate species by BC amendments (Ahmad et al. 2014b). In particular, Ahmad et al. (2016) confirmed the formation of highly stable chloropyromorphite ($Pb_5(PO_4)_3Cl$) in a shooting range soil amended with soybean stover- and pine needle-derived BCs by using an extended x-ray absorption fine structure (EXAFS) spectroscopy. By contrast, no such Pb-phosphate mineral was predicted by the model in the BC treated agricultural soil while stable Zn-phosphate minerals were predicted in SS-BC300, SS-BC700 and PN-BC700 treated agricultural soils (i.e., consistent with Zn immobilization shown in Fig. 6). In addition, strong positive correlations were observed between heavy metals (Pb, Zn, and Cu), and Fe and Al (Fig. 7), signifying that surface complexation was also plausible between metals and Fe- and Al-hydroxides (i.e., mineral components) of BCs. This corroborated the significance of amendments containing high contents of Fe- and Al-hydroxides for the metals immobilization (Usman et al. 2006).

The results of PCA of metals and metalloids in the shooting range and agricultural soils (Fig. 8) indicated that F1 negatively correlated with Pb, Zn, and Cu concentrations while positively correlated with As and Sb concentrations. This may infer that EC and dissolved total C in BC amended soils were correlated with metal immobilization, whereas PO_4 and SO_4 were involved in metalloid mobilization. This was also confirmed by positive linear correlations between PO_4 and As in the agricultural soil ($R^2 = 0.811$) and Sb in the shooting range soil ($R^2 = 0.694$), respectively (data not shown).

Therefore, in the alkaline shooting range soil, surface complexation of Pb and Cu with -COOH functional groups and Fe-/Al-minerals of BCs as well as Pb-/Cu-phosphate precipitation were primarily accountable for their immobilization, whereas in the acidic agricultural soil, BC induced pH increase was the main factor for immobilizing Pb and Zn via metal-hydroxides precipitation. It is noted that electrostatic attraction and cation exchange (Uchimiya et al. 2011) as well as π-π electron donor-acceptor interaction (Sun et al. 2012) may contribute to immobilization to some extent, which is, however, difficult to quantify. On the contrary, in both soils, solubilization of As and Sb into soil solution was unfavorably enhanced by PO_4 competition and electrostatic repulsion, both of which were aggravated by amendment with alkaline and PO_4-containing BCs.

In a view of the spectrum of mechanisms controlling metal immobilization and metalloid mobilization, the soil and BC types as well as the corresponding changes in ionic properties of soil-BC systems play an important role. This study suggests that BC should be applied with great caution to multi-metal contaminated soil where it may cause contradictory effects, and that BC should be tailored to accomplish desired outcome and avoid any negative impact on soil ecosystem.

4 Conclusions

Biochars produced from three different waste feedstocks at two pyrolysis temperatures exhibited variable characteristics that accordingly influenced the soil properties and their efficiency towards metals/metalloids immobilization/mobilization in the contaminated soils. All BCs exponentially increased the ionic contents of shooting range and agricultural soils. Cationic heavy metals (Pb, Zn, and Cu) were immobilized while anionic metalloids (As and Sb) were mobilized by amendment with BCs in both soils. Multiple mechanisms including surface complexation and precipitation contributed to metals immobilization while electrostatic repulsion and phosphate competition were involved in metalloids mobilization. We conclude that all BCs behave distinctively in different types of contaminated soils. Therefore, BCs should be customized under well-controlled and engineered pyrolysis conditions for its optimum performance in different soils.

Acknowledgments This study was supported by the National Research Foundation of Korea (NRF-2015R1A2A2A11001432).

References

Ahmad M, Hashimoto Y, Moon DH, Lee SS, Ok YS (2012a) Immobilization of lead in a Korean military shooting range soil using eggshell waste: an integrated mechanistic approach. J Hazard Mater 209–210:392–401

Ahmad M, Lee SS, Dou X, Mohan D, Sung JK, Yang JE, Ok YS (2012b) Effects of pyrolysis temperature on soybean stover- and peanut shell-derived biochar properties and TCE adsorption in water. Bioresour Technol 118:536–544

Ahmad M, Lee SS, Moon DH, Yang JE, Ok Y (2012c) A review of environmental contamination and remediation strategies for heavy metals at shooting range soils. In: Grohmarin E, Malik A (eds) Environmental protection strategies for sustainable development. Springer, Netherlands, pp 437–451

Ahmad M, Moon DH, Lim KJ, Shope CL, Lee SS, Usman ARA, Kim KR, Park JH, Hur SO, Yang JE, Ok YS (2012d) An assessment of the utilization of waste resources for the immobilization of Pb and

Cu in the soil from a Korean military shooting range. Environ Earth Sci 67:1023–1031

Ahmad M, Lee SS, Lim JE, Lee SE, Cho JS, Moon DH, Hashimoto Y, Ok YS (2014a) Speciation and phytoavailability of lead and antimony in a small arms range soil amended with mussel shell, cow bone and biochar: EXAFS spectroscopy and chemical extractions. Chemosphere 95:433–441

Ahmad M, Rajapaksha AU, Lim JE, Zhang M, Bolan N, Mohan D, Vithanage M, Lee SS, Ok YS (2014b) Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 99:19–33

Ahmad M, Ok YS, Rajapaksha AU, Lim JE, Kim BY, Ahn JH, Lee YH, Al-Wabel MI, Lee SE, Lee SS (2016) Lead and copper immobilization in a shooting range soil using soybean stover- and pine needle-derived biochars: chemical, microbial and spectroscopic assessments. J Hazard Mater 301:179–186

Al-Tabbaa A, Perera ASR (2006) UK stabilization/solidification treatment and remediation-part I: binders, technologies, testing and research. Land Contam Reclam 14:1–22

Al-Wabel MI, Al-Omran A, El-Naggar AH, Nadeem M, Usman ARA (2013) Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus waste. Bioresour Technol 131:374–379

Beesley L, Jimenez EM, Eyles JLG (2010) Effects of biochar and green waste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. Environ Pollut 158:2282–2287

Beesley L, Marmiroli M, Pagano L, Pigoni V, Fellet G, Fresno T, Vamerali T, Bandiera M, Marmiroli N (2013) Biochar addition to an arsenic contaminated soil increases arsenic concentrations in the pore water but reduces uptake to tomato plants (*Solanumlycopersicum* L.). Sci Total Environ 454–455:598–603

Bolan N, Kunhikrishnan A, Thangarajan R, Kumpiene J, Makino T, Kirkham MB, Scheckel K (2014) Remediation of heavy metal(-loid)s contaminated soils—to mobilize or to immobilize? J Hazard Mater 266:141–166

Brebu M, Vasile C (2010) Thermal degradation of lignin—a review. Cellul Chem Technol 44:353–363

Busch D, Glaser B (2015) Stability of co-composted hydrochar and biochar under field conditions in a temperate soil. Soil Use Manag 31: 2511–258

Cabrera A, Cox L, Spokas K, Hermosin MC, Cornejo J, Koskinen WC (2014) Influence of biochar amendments on the sorption–desorption of aminocyclopyrachlor, bentazone and pyraclostrobin pesticides to an agricultural soil. Sci Total Environ 470–471:438–443

Cao X, Ma LQ, Chen M, Hardison DW, Harris WG (2003) Weathering of lead bullets and their environmental effects at outdoor shooting ranges. J Environ Qual 32:526–534

Clemente R, Dickinson NM, Lepp NW (2008) Mobility of metals and metalloids in a multi-element contaminated soil 20 years after cessation of the pollution source activity. Environ Pollut 155:254–261

Clemente R, Hartley W, Riby P, Dickinson NM, Lepp MW (2010) Trace element mobility in a contaminated soil two years after field-amendment with a green waste compost mulch. Environ Pollut 158:1644–1651

Crombie K, Masek O (2015) Pyrolysis biochar systems, balance between bioenergy and carbon sequestration. GCB Bioenergy 7:349–361

Fang ZF, Liu KL, Chen FS, Zhang LF, Guo Z (2014) Cationic surfactant-assisted microwave-NaOH pretreatment for enhancing enzymatic hydrolysis and fermentable sugar yield from peanut shells. Bioresources 9:1290–1302

Giudicianni P, Cardone G, Ragucci R (2013) Cellulose, hemicellulose and lignin slow steam pyrolysis: thermal decomposition of biomass components mixtures. J Anal Appl Pyrolysis 100:213–222

Hashimoto Y, Taki T, Sato T (2009) Extractability and leachability of Pb in a shooting range soil amended with poultry litter ash: Investigations for immobilization potentials. J Environ Sci Health A 44:583–590

Herath I, Kumarathilaka P, Navaratne A, Rajakaruna N, Vithanage M (2015) Immobilization and phytotoxicity reduction of heavy metals in serpentine soil using biochar. J Soils Sediments 15: 126–138

IBI (2012) Standardized product definition and product testing guidelines for biochar that is used in soil. Int Biochar Initiative, 2012

Iqbal M, Saeed A, Edyvean RGJ (2013) Bioremoval of antimony(III) from contaminated water using several plant wastes: optimization of batch and dynamic flow conditions for sorption by green bean husk (*Vigna radiate*). Chem Eng J 225:192–201

Klasson KT, Uchimiya M, Lima IM (2014) Uncovering surface area and micropores in almond shell biochars by rainwater wash. Chemosphere 111:129–134

Lim JE, Ahmad M, Usman ARA, Lee SS, Jeon WT, Oh SE, Yang JE, Ok YS (2013) Effects of natural and calcined poultry waste on Cd, Pb and As mobility in contaminated soil. Environ Earth Sci 69:11–20

Mench M, Vangronsveld J, Lepp N, Ruttens A, Bleeker P, Geebelen W (2007) Use of soil amendments to attenuate trace element exposure: sustainability, side effects, and failures. In: Hamon R, McLaughlin MJ, Lombi E (eds) Natural attenuation of trace element availability in soils. SETAC Press, CRCTaylor & Francis, Pensacola, pp 197–228

Merry RH (2010) Acidity and alkalinity of soils. In: Sabljic A (ed) Environmental and ecological chemistry, vol 2. UNESCO EOLSS, UK

MOE (2010) Soil environment conservation act. Ministry of Environment, Republic of Korea

Mohan D, Sarswat A, Ok YS, Pittman CU Jr (2014) Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent—a critical review. Bioresour Technol 160:191–202

Ok YS, Oh SE, Ahmad M, Hyun S, Kim KR, Moon DH, Lee SS, Lim KJ, Jeon WT, Yang JE (2010) Effects of natural and calcined oyster shells on Cd and Pb immobilization in contaminated soils. Environ Earth Sci 61:1301–1308

Olive IX (2006) Mobility of lead and antimony in shooting range soils. PhD thesis ETH No. 16689. Swiss Federal Institute of Technology, Zurich

Rajapaksha AU, Ahmad M, Vithanage M, Kim KR, Chang JY, Lee SS, Ok YS (2015) The role of biochar, natural iron oxides, and nanomaterials as soil amendments for immobilizing metals in shooting range soil. Environ Geochem Health 37:931–942

Rinklebe J, Shaheen SM (2015) Miscellaneous additives can enhance plant uptake and affect geochemical fractions of copper in a heavily polluted riparian grassland soil. Ecotoxicol Environ Saf 119:58–65

Silveria MLA, Alleoni LRF, Guilherme LRG (2003) Biosolids and heavy metals in soils. Sci Agric 60:793–806

Sparks DL, Page AL, Helmke PA, Loeppert RH, Soltanpour PN, Tabatabai MA, Johnston CT, Summer ME (1996) Methods of soil analysis. Part 3 chemical methods. Soil Science Society of America Inc, Madison

Sun K, Jin J, Keiluweit M, Kleber M, Wang Z, Pan Z, Xing B (2012) Polar and aliphatic domains regulate sorption of phthalic acid esters (PAEs) to biochars. Bioresour Technol 118:120–127

Tsang DCW, Yip ACK (2014) Comparing chemical-enhanced washing and waste-based stabilisation approach for soil remediation. J Soils Sediments 14:936–947

Tsang DCW, Olds WE, Weber PA, Yip ACK (2013) Soil stabilisation using AMD sludge, compost and lignite: TCLP leachability and continuous acid leaching. Chemosphere 93:2839–2847

Tsang DCW, Yip ACK, Olds WE, Weber PA (2014) Arsenic and copper stabilisation in a contaminated soil by coal fly ash and green waste compost. Environ Sci Pollut Res 21:10194–10204

Uchimiya M, Chang S, Klasson KT (2011) Screening biochars for heavy metal retention in soil: role of oxygen functional groups. J Hazard Mater 190:432–441

Uchimiya M, Bannon DI Wartelle LH, Lima IM, Klasson KT (2012) Lead retention by broiler litter biochars in small arms range soil: impact of pyrolysis temperature. J Agric Food Chem 60:5035–5044

Usman ARA, Kuzyakov Y, Stahr K (2006) Remediation of a soil contaminated with heavy metals by immobilizing compounds. J Plant Nutr Soil Sci 169:205–212

Violante A, Cozzolino V, Perelomov L, Caporale AG, Pigna M (2010) Mobility and bioavailability of heavy metals and metalloids in soil environments. J Soil Sci Plant Nutr 10:268–292

Wuana RA, Okieimen FE (2011) Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. ISRN Ecology 2011:402647

Yao Y, Gao B, Zhang M, Inyang M, Zimmerman AR (2012) Effect of biochar amendment on sorption and leaching of nitrate, ammonium, phosphate in a sandy soil. Chemosphere 89:1467–1471

Yuan JH, Xu RK, Zhang H (2011) The forms of alkalis in biochar produced from crop residues at different temperatures. Bioresour Technol 102:3488–3497

Zhang J, Liu J, Liu R (2015) Effects of pyrolysis temperature and heating time on biochar obtained from the pyrolysis of straw and lignosulfonate. Bioresour Technol 176:288–291