Environ Sci Pollut Res (2016) 23:2381–2390
DOI 10.1007/s11356-015-5458-7

RESEARCH ARTICLE

Organic amendments impact the availability of heavy metal(loid)s in mine-impacted soil and their phytoremediation by *Penisitum americanum* and *Sorghum bicolor*

Javed Nawab[1,2,3] · **Sardar Khan**[1,2] · **Muhammad Aamir**[2,3] · **Isha Shamshad**[2,4] · **Zahir Qamar**[2] · **Islamud Din**[4] · **Qing Huang**[1]

Received: 1 August 2015 / Accepted: 17 September 2015 / Published online: 28 September 2015

Abstract The amendment of contaminated soil with organic materials is considered to be an environmentally friendly technique to immobilize heavy metal(loid)s and minimize their subsequent bioaccumulation in plants. This study focuses on the effects of different amendment techniques, such as the use of activated carbons (granulated or powder) and farmyard manure at various application rates (2 and 5 %). These techniques were applied on heavy metal(loid)s such as Ni, Cr, Cd, Pb, Mn, Cu, Zn, Fe, Co, and Al that were present in mine-impacted soil and caused bioaccumulation in cultivated plants. The results showed that, compared with the control, almost all the techniques significantly ($P \leq 0.01$) reduced the bioavailability of heavy metal(loid)s in the amended soil. The bioaccumulation of heavy metal(loid)s in *Penisitum americanum* and *Sorghum bicolor* was significantly ($P \leq 0.01$) reduced with all techniques, while Zn and Cd concentrations increased with the use of farmyard manure. Also compared with the control, plant growth was significantly decreased with the use of activated carbons, particularly with powder activated carbons, while farmyard manure (at 5 %) significantly ($P \leq 0.01$) increased plant growth. Among the amendment techniques, powdered activated carbons (at 5 %) were best at reducing the bioavailability of heavy metal(loid)s in soil and plant accumulation. However, it negatively affected the growth of selected plant species.

Keywords Bioaccumulation · Amendments · Immobilize · Mine-impacted soil · Plant yield · Heavy metal(loid)s

Introduction

The soil ecosystem, which is contaminated with heavy metal(loid)s, is considered to be a global environmental issue. Heavy metal(loid)s have both natural (ore deposit or weathering/erosion of parent rocks) and manmade sources (mining, electroplating, energy, smelting power transmission, fuel production, sludge dumping, intensive agriculture, waste water irrigation, and dust) (Khan et al. 2015; Nawab et al. 2015a; Chanpiwat et al. 2010; Wei and Yang 2010). Mining-impacted soils are classified as poorly structured soils and lack vegetative cover due to the high toxicity associated with heavy metal(loid)s (Nawab et al. 2015b; Mench et al. 2010). In previous research, organic amendments have been used to either immobilize or mobilize heavy metal(loid)s in contaminated soils (Khan et al. 2015; Ahmad et al. 2012). In the mobilization technique, the metal(loid)s are released into the soil and are subsequently removed through the native plant species. For the immobilization technique, the metal(loid)s are rendered unavailable for plant uptake, human ingestion, and leaching into groundwater from the soil through adsorption,

---

Responsible editor: Zhihong Xu

Electronic supplementary material The online version of this article (doi:10.1007/s11356-015-5458-7) contains supplementary material, which is available to authorized users.

✉ Sardar Khan
sardar.khan2008@yahoo.com

✉ Qing Huang
qhuang@iue.ac.cn

[1] Key Laboratory of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, China

[2] Department of Environmental Sciences, University of Peshawar, Peshawar 25120, Pakistan

[3] Department of Environmental and Conservation Sciences, University of Swat, Swat 19130, Pakistan

[4] Department of Environmental Sciences, International Islamic University, Islamabad, Pakistan

the formation of complex compounds, and precipitation reactions (Bolan et al. 2003). Activated carbon (AC) is generally prepared by heating carbonaceous material at a high temperature (above 600 °C) for a long period of time (>10 h) to make it extremely porous, resulting in a very high adsorptive capacity (Tomaszewski et al. 2007). Several organic materials are used to increase immobilization of heavy metal(loid)s, but AC is extremely efficient (Ucer et al. 2006; Lima and Marshal 2005).

Previously, Lyubchik et al. (2008) reported that AC was very effective in the removal of heavy metal(loid)s (50–55 %) by the precipitation of metal hydroxide and the adsorption of metal cation (15–20 %) on the negatively charged surfaces of AC. While AC is commonly used for the removal of heavy metal(loid)s from wastewater, its effects on metal immobilization in contaminated soil is rarely studied and still needs further research.

Activated carbon is a proficient and environmentally friendly material used for the removal of heavy metal(loid)s, particularly from industrial effluent (de Lima et al. 2014). AC, liquid organic fertilizers, and attapulgite clay amendments immobilize diethylene triamine pentaacetic acid (DPTA) extractable metals in soil that also affect the plant growth (Liu et al. 2012). AC has a high adsorption capacity for heavy metal(loid)s and can therefore remove more than 90 % of metal(loid)s such as Cu, Co, Cr, Mn, and Fe from landfill leachate compared with the control (Modin et al. 2011). The concentrations of organic pollutants can also be reduced by the addition of a small amount of AC into the contaminated environmental matrices (Brandli et al. 2008; Zimmerman et al. 2004). AC has a high sorption capacity due to its unique chemical composition, high porosity, and large surface area. The strong sorption capacity of AC has been shown to reduce contaminant accessibility to microorganisms (Rhodes et al. 2008). AC, both in powder (ACP) and granulated (ACG) forms, affects the growth of plants and reduces the availability of organic contaminants such as polycyclic aromatic hydrocarbons (Jakob et al. 2012). AC act as a promoter of embryogenesis in the microscopic culture of various pepper genotypes at 0.05 % concentration, while the low responsive genotype showed the most significant effect (Cheng et al. 2013).

Published literature has shown that organic amendment techniques reduced heavy metal(loid)s such as Cd, As, Pb, Cu, Zn, and Cr in the soil (Bolan et al. 2014). The farmyard manure (FYM) amendment is known to convert Cr (VI) to Cr (III), which is less toxic and mobile (Bolan et al. 2003). Most manure byproducts have comparatively low concentrations of toxic metal(loid)s and can therefore be used to immobilize these metal(loid)s in contaminated soils. Several other organic amendments such as composts, bio-solids, or bio-solid compost have effectively reduced the concentrations of heavy metal(loid)s in amended soils (Ahmad et al. 2014). Gupta et al. (2008) investigated the efficiency of 2 % FYM application and observed that the bioaccumulated concentrations of Ni decreased by 39, 40, 45, and 35 % in carrot, fenugreek, spinach, and wheat grain, respectively.

The aim of this work is to investigate the influence of ACP, ACG, and FYM amendments on the availability of heavy metal(loid)s in mine-impacted soil and their bioaccumulation in plants. Two types of fodder plant species (*Penisitum americanum* and *Sorghum bicolor*) were cultivated in mine-impacted soil amended with the selected organic materials. This was performed at different application rates for the purpose of studying the impact of these amendments on the phytoremediation of heavy metal(loid)s, such as As, Cd, Cr, Cu, Ni, Zn, Pb, Co, Mn, Al, and Fe. The effect of amendments on plant growth was also investigated.

Ethics statement

The collection of soil samples from mine sites is not a restricted activity. Therefore, no permission from any organization was required to collect soil for these control experiments. Moreover, no endangered or protected species were involved in this study. The cultivation of the selected plant seedlings did not require any permission.

Materials and methods

Chemical materials

Three types of organic materials, ACP, ACG, and FYM, were used for control experiments. The ACP and ACG were purchased from Norit Nederland BV Amersfoort. The particle size of ACP ranged from 1 to 150 μm, while ACG ranged from 1 to 3 mm. Locally produced FYM (cow manure) was used in this research. Certified seeds of fodder plant species *P. americanum* and *S. bicolor* were purchased from The Agriculture Research Center, Takhtaband Swat, Pakistan. All chemicals used were analytical grade and purchased from Merck (Merck KGaA, 64271 Darmstadt, Germany).

Soil sampling and preparation

Heavy metal(loid) contaminated soil (120 kg) was collected from 0–20 cm depth of mining-impacted sites in Khyber Pukhtunkhwa, Pakistan. The collection of soil samples from mine sites is not a restricted activity. Therefore, no permission from any organization was required to collect soil for these control experiments. First, the soil was air dried, sieved (2 mm), and homogenized into a single composite sample. The sub-sample was then stored in a paper envelope at 20 °C. The physico-chemical properties of the soil, including pH, texture, and electrical conductivity (EC), were determined (Table 1) using standard procedures (Waqas et al. 2014). The soil particle size distribution was sand (66 %), silt (16 %), and clay (18 %).

Experimental design

The selected organic materials (ACP, ACG, and FYM) were homogenously mixed (at 2 and 5 % application rates) with the chromate mine-impacted soil on a dry weight (dw) basis. The samples were then defined as ACP2, ACP5, ACG2, ACG5, FYM2, and FYM5. All the amended (with organic materials) and control treatments (without organic materials) were prepared in triplicate. The fertilizers, such as NH_4NO_3 (120 mg N/kg soil) and K_2HPO_4 (30 mg P/kg soil and 75.7 mg K/kg soil), were thoroughly mixed with all the treatments (Khan et al. 2013). Each plastic pot was filled with 2.5 kg of sample and irrigated with deionized water. Two sets of each treatment were prepared: one set was cultivated with *P. americanum* and the other with *S. bicolor* (ten seeds in each pot). These were not endangered or protected species and their cultivation did not require any permission. These experiments were conducted in a greenhouse for 3 months, and the pots were regularly irrigated with deionized water

Table 1 Basic characteristics of ACP, ACG, FYM, and soil used in this study compared with the permissible limits set by SEPA (1995)

Properties	Activated carbon powder	Activated carbon granules	Farmyard manure	Mine-impacted soil	SEPA soil limits
pH	7.5	7.2	7.3	7.1	
EC (μS/cm)	564	551	382	352	
Mean total concentration (mg/kg) of heavy metal(loid)s					
(Dry-weight basis *n*=3)					
C (%)	49	40	3.65	2.12	–
N (%)	3	2.3	12.8	0.42	
S (%)	2.2	1.84	2.01	0.09	
P	26.5	28.7	33.8	21.1	
Ni	3.40	3.75	6.21	345	40
As	BDL[a]	0	0.001	7.92	40
Cd	BDL	0	0.1	1.20	0.3
Cr	0.02	0.03	0.52	654	150
Co	0	0	0.04	24	–
Pb	0	0	0.21	16	250
Cu	3.96	4.45	4.23	35	50
Fe	970	1078	40	24,348	–
Al	0	0	0.05	10,522	–
Zn	6	7.21	9.4	82	200
Mn	0.48	0.52	6	410	-
Mean bioavailable concentration (mg/kg) of heavy metal(loid)s					
(Dry-weight basis *n*=3)					
Ni	0.02	0.03	1.04	16	
As	BDL	0	0	0.8	
Cd	0	0	0.04	0.7	
Cr	0.005	0.001	0.09	27.25	
Co	0	0	0	6.25	
Pb	0	0	0.03	5.68	
Cu	0.36	0.75	0.95	14.20	
Fe	9	12	5.67	824	
Al	0	0	0.001	190	
Zn	1.6	2.45	2.42	45	
Mn	0.006	0.01	0.84	29.74	

[a] Below detection limits

to keep the water content at 60 %. Upon maturity, the *P. americanum* and *S. bicolor* plants were harvested and dried in an oven at 70 °C for 72 h. Dry weights of the roots and shoots were recorded.

Chemical analyses

A strong acid extraction method was used to determine total heavy metal(loid) concentrations for all treatments (amended and control soils). Oven-dried samples (1.0 g) of each material were digested in a Teflon beaker with a mixture of strong acids $HNO_3/HClO_4$ (3:1, *v*/*v*) at 70–80 °C. The solution was allowed to evaporate by raising the temperature to 105 °C until the solution became transparent. After filtration, the final volume of extract was made up to 50 ml with 0.1 N HNO_3. Heavy metal(loid) concentrations in the powder fodder plants were investigated according to the method adopted by Ryan et al. (2001). Concentrated HNO_3 was used to digest 1.0 g of each plant sample. After filtration, deionized water was used to make the final volume up to 50 ml. To investigate the bioavailable heavy metal(loid)s in ACP, ACG, FYM, the soil, and their amendments (ACP/ACG/FYM), a mixture of reagents comprising EDTA-Na_2 (0.05 M), $CaCl_2$ (0.01 M), and tri-ethanolamine (0.1 M) was used according to the method adopted by Zeng et al. (2011). The concentrations of Al and Fe were determined using ICP-OES (Perkin Elmer Optima 7000 DV, USA), while As, Cr, Cd, Pb, Ni, Mn, Cu, Zn, and Co concentrations were measured using ICP-MS (Agilent Technologies, 7500 CX, USA) at the Institute of Urban Environment, Xiamen, China.

Quality control

To check for contamination in the digestion and analysis processes, reagent blanks were included in each batch. The standard reference materials of plant (GBW-07602 (GSV-1)) that belonged to shrub and soil (GBW-07406 (GSS-6)) were purchased from the National Research Center for Standards in China and were included for recovery efficiency from the digestion process. The recovery rates of selected metal(loid)s were observed in the range of 91.5±8.4 % to 103±6.5 %.

Data analysis

For data analysis, the statistical package SPSS (version 21; IBM Corporation, USA) was used. The mean, standard deviation, and variance of the triplicates were determined using ANOVA.

Results and discussion

Characteristics of soil and organic materials

The basic properties of the organic materials (ACP, ACG, and FYM) and mine-impacted soil used in this research are given in Table 1. These selected organic amendments show differences in soil physical properties, such as pH and EC. The highest soil pH (at 8.1) was observed for ACP5, followed by ACP2 (at 7.8). The lowest pH (at 7.3) was observed for FYM2. Compared with the control, almost all the amendments resulted in an increase in soil pH. The concentrations of each heavy metal(loid) in the mine-impacted soil, ACP, ACG, and FYM are given in Table 1.

The initial pH of the mine-impacted soil was 7.1, while the corresponding EC value was 352 μS/cm (Table 1). The total metal concentrations of Cd (1.2 mg/kg), Ni (345 mg/kg), and Cr (654 mg/kg) in the soil were higher than the respective maximum guidance limits set by the State Environmental Protection Administration, China (SEPA 1995). However, the total concentrations of Pb, As, Zn, and Cu were found to be within their maximum guidance limits set by SEPA (1995).

Effects of organic amendments on soil heavy metal(loid)s

The total and bioavailable concentrations of heavy metal(loid)s in the amended soil (compared to the control) for all the organic amendments (ACP2, ACP5, ACG2, ACG5, FYM2, and FYM5) decreased (Table 2). The decrease in bioavailable concentrations of the respective metal(loid)s in ACP (2 and 5 %) amendments were observed (Table 2). These findings indicate that ACP amendments caused the lowest reduction in the availability of As followed by Cd, which could be linked with highly mobile properties of these elements (Dobran and Zagury 2006). In the ACP-amended soil, the highest reduction was observed in the available concentration of Co followed by Zn. Similarly, the concentrations of metal(loid)s in the ACG-amended soils (2 and 5 %) decreased as shown in Table 2. The treatments of ACG also showed the lowest influence on the immobilization of As and Cd in the amended soil. However, the effectiveness of ACP was comparatively greater than ACG. In FYM (2 and 5 %) amendments, the decrease in available metal(loid) concentrations were Cd (−1.42 and −4 %), Zn (−15 and −11 %), Cu (−11 and −20 %), Cr (−2 and −8 %), Ni (−8 and −13 %), Mn (−12 and −15 %), Fe (−7 and −12 %), Co (−1.2 and −3 %), Pb (−8 and −15 %), As (0 and −4 %), and Al (−18 and −24 %) (Table 2). The detailed information is given in the Supporting Information (Table S2) document.

Based on these results, ACP (2 and 5 %) was more efficient in reducing the available concentrations of heavy metal(loid)s. The decrease observed in ACP-amended soil was significantly ($P \le 0.01$) higher compared to ACG2, ACG5, FYM2, FYM5,

Table 2 The characteristics of control and ACP-, ACG-, and FYM-amended soils (n=3)

Parameters	Control	ACP2	ACP5	ACG2	ACG5	FYM2	FYM5
pH	7.1	7.8	8.1	7.4	7.6	7.3	7.5
EC (μS/cm)	352	389	462	367	415	343	356
C (%)	2.12	12	26.6	10.1	22.1	2.85	3.94
N (%)	0.42	1.02	1.92	0.88	1.57	2.97	6.81
S (%)	0.09	0.53	1.19	0.46	1.01	0.49	1.09
P (mg/kg)	21.1	18.8	16.5	20.5	24.2	23.6	27.4
Mean total heavy metal(loid) concentrations (mg/kg dw)							
Ni	345	202	94	295	210	312	262
As	8	3	2.7	6.7	4.47	7.2	6.5
Cd	1.2	0.59	0.45	0.75	0.55	0.88	0.82
Cr	654	390	98	608	461	626	585
Co	24	17	8.4	22	17	22	20
Pb	16	13.45	8	15	13.9	14.4	13.6
Cu	35	25	14	29	26	31	27
Fe	24348	22426	21735	23677	22303	24004	22850
Al	10522	10037	9547	10432	9926	10486	10245
Zn	82	71	55	75	67	79	75
Mn	410	258	101	372	285	396	371
Mean bioavailable concentration (mg/kg dw) of selected metal(loid)s							
Ni	16	10.7	8.2	13.8	11.6	14.7	14.0
As	0.8	0.77	0.6	0.79	0.72	0.8	0.77
Cd	0.7	0.53	0.48	0.6	0.5	0.69	0.67
Cr	27	18.3	13.2	21.2	19.8	26.5	24.8
Co	8.2	2.75	1.88	6.8	5.2	8.1	7.90
Pb	5.7	3.89	2.95	4.5	4	5.25	4.85
Cu	14	11	8.2	12.3	10.5	12.4	11.2
Fe	824	357	289	553	487	765	722
Al	190	100	75	180	138	156	145
Zn	45	21	17	27	23.7	38	40
Mn	30	21.1	15.8	23.2	21.4	26.3	25.5

dw dry weight

and the control treatments. ACP had a comparatively smaller particle size (1–150 μm) than ACG (1–3 mm), as shown in Table 1. Water retention showed a strong relationship with capillary forces in the soil and provided metal solubility to the plants (Jakob et al. 2012). The ACP-amended soil capillary force was higher than the control, FYM-amended, and ACG-amended soil, thereby showing lower water availability and fewer pore spaces (Jakob et al. 2012). Soil pH plays a very important role in metal availability in soil and their bioaccumulation in plants. At soil pH greater than 6, the concentrations of free metal ions in solution decrease due to organic matter chelation, oxide surface charge enhancement, and metal hydroxide precipitation (Khan et al. 2015; Mouta et al. 2008). Precipitation processes occur between metals and anions such as OH^{-}, SO_4^{2-}, HPO_4^{2-}, and CO_3^{2-}. This process is considered to be one of the most important mechanisms for reducing the mobility of toxic metal(loid)s in soil amended with organic materials such as AC, FYM, and biochar (Ok et al. 2010). At higher pH values, different functional groups such as carbonyl, phenolic, carboxyl, and alcohol isolate organic materials were used for soil amendment. This, in turn, increases the affinity between the functional groups and metal ions (Khan et al. 2015; Ahmad et al. 2014; McGowen et al. 2001). The high concentration of P in organic matter such as FYM also reduces metal mobility through the precipitation. In previous studies, P showed a reduction in the leaching of toxic metals such as Cd, Pb, and Zn (Bolan et al. 2014). In acidic soil, the addition of organic materials, such as composts and manures, increases the soil pH, which reduces the metal availability in the soil (Walker et al. 2004). In this research, the soil pH decreased from 2.9 to 14.1 % in the organic amended soils. Compared with the control, the highest effect was observed in the ACP5 treatment followed by the ACP2 (Table 1). FYM also reduced soil pH (by 0.2–0.4) and showed effectiveness in metal availability. However, Davis and Wilson (2005) suggested that aged manure should be used for soil remediation purposes because fresh manure contains high ammonia contents, which can harm the plants. The changes in other basic properties, such as dissolved organic carbon (DOC) and EC, can also affect the availability of metals in the amended soil (Khan et al. 2013; Violante et al. 2010).

Walker et al. (2004) and Castaldi et al. (2005) have observed a decrease in heavy metal(loid) concentrations in plant shoots grown in amended soil compared with the control. Different organic composts such as biosolid, municipal solid waste, and manure have been used by various scientists for heavy metal (loid) adsorption in contaminated soils (Clemente et al. 2007; Cala et al. 2005; Rate et al. 2004; Walker et al. 2004; Cao and Ma 2004; Cao et al. 2003). In the majority of the experiments, the amendments decreased the heavy metal(loid) uptake by plants.

Effect of the organic amendments on plant biomass

The biomass of *P. americanum* was reduced significantly ($P<0.01$) in ACP- and ACG-amended soils compared with the control (Fig. 1). ACP treatments showed a decrease from 69 to 75 %, while ACG decreased from 16 to 19 %. Inconsistently, the biomass of the plant was increased with the amendment of FYM compared with the control. The FYM treatments increased the biomass of *P. americanum* from 10 to 20 % compared with the control (Fig. 1). Similarly, the *S. bicolor* biomass decreased with the amendments of ACP (27–64 %) and ACG (4–24 %), while it increased with FYM treatments (11–26 %) compared with the control (for details see S1). These results show that the addition of FYM increases plant biomass. This increase may be due to the availability of nutrients (predominantly nitrogen) produced by the decay of FYM (Clemente et al. 2007; Nwachukwu and Pulford 2009). Higher amendments of FYM produced a higher biomass, which may be due to the release of additional nutrients, an improved buffering capacity, and enhanced nutrient cycling upon decomposition of farm manure (Clemente et al. 2007; Stewart et al. 2000; Liu et al. 2009).

The plant biomass and growth are mostly dependent on the soil's physical and chemical parameters and, especially, the availability of water, nutrients, and oxygen. The ACG-amended soil may have aerobic conditions due to its coarse structure (1–3 mm size of particle), while the ACP may have less aerobic condition due to its compact structure (1–150 μm) (Glaser et al. 2002). Thus, ACP amendment compacted the soil and reduced aeration. These conditions affect aerobic bacteria and root penetration in the amended soil (Jakob et al. 2012). The improved plant biomass in ACG amendments can be attributed to an improvement in soil aeration and structure compared with ACP. Organic amendment usually improves the fertility of soil and enhances plant growth and biomass (Khan et al. 2015; Walker et al. 2004; Williamson and Johnson 1981). Heavy metal(loid)s are reduced in organic amendment soils by converting available fractions into those linked with organic matter, carbonates, and metal oxides (Walker et al. 2004). In the present research, FYM5 amendments significantly ($P<0.01$) improved the selected plant biomasses compared with the control. These significant increases in biomass can be linked with higher concentrations of nutrients (mainly nitrogen) and the improvement in the buffering capacity of the soil amended with FYM5 materials (Clemente et al. 2007; Stewart et al. 2000; Liu et al. 2009; Nwachukwu and Pulford 2009).

Heavy metal(loid) bioaccumulation in plants

The bioaccumulation of metal(loid)s in the plant shoots was determined (Fig. 2). The ACP, ACG, and FYM amendments significantly reduced the bioaccumulation of metal(loid)s in *P. americanum* and *S. bicolor*. The effects of organic amendments on the bioaccumulation of heavy metal(loid)s in selected plants varied greatly. The concentrations of all the selected heavy metal(loid)s (except Zn and Cd with FYM5, FYM2) were reduced in the shoots of *P. americanum* grown in the amended soils compared with the control. Similar trends in reduction of metal bioaccumulation were also observed in *S. bicolor* shoots grown in ACP-, ACG-, and FYM-amended soils (Fig. 3).

For *P. americanum*, the highest average decrease was observed in bioaccumulation of Ni (from 38 to 69 %), followed by As (from 38 to 49 %) in ACP-amended soil. For ACG2 and ACG5 applications, the highest average decrease was observed for Ni (from 30 to 43 %), followed by Cr (from 27 to 41 %), as shown in Fig. 2. For FYM2 and FYM5 applications, the highest decrease was observed in bioaccumulation of Ni (from 19 to 38 %), followed by Cr (from 24 to 37 %), while the concentrations of Cd and Zn increased (from 5 to 18 % and from 21 to 35 %, respectively) within soil amended with FYM (for detail see S3).

For *S. bicolor*, the highest average decrease was observed in the bioaccumulation of As (from 48 to 73 %), followed by Ni (from 46 to 64 %) in ACP treatments; in ACG2 and ACG5 treatments, the highest average decrease was observed for Ni (from 40 to 49 %), followed by Cu (from 36 to 50 %). For FYM2 and FYM5 applications, the highest average decrease was observed for Ni (from 28 to 48 %), followed by Cu (from 29 to 40 %), while the Cd and Zn concentrations increased from 3 to 8 %, and from 26 to 44 %, respectively, as presented in Fig. 3 (for detail see S4).

The aforementioned results indicate that all the amendments (ACP, ACG, and FYM) reduced the heavy metal(loid) (Ni, Pb, As, Co, Fe, Cu, Cr, Al, and Mn) bioaccumulation in the shoots of *P. americanum* and *S. bicolor*.

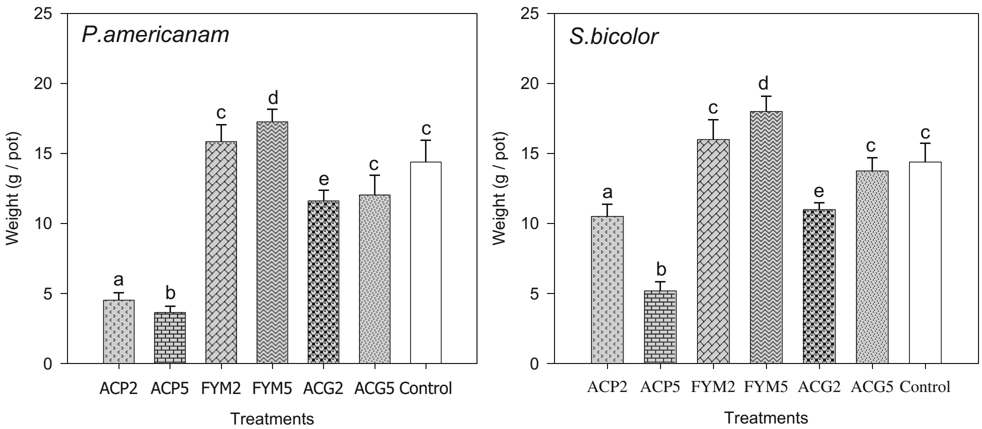

Fig. 1 The effects of ACP, ACG, and FYM amendments (2 and 5 %) on *P. americanum* and *S. bicolor* biomass yields. *Error bars* represent standard deviation. Similar *letters* indicate no significant difference ($P \leq 0.01$), while different *letters* indicate significant differences compared with the control experiment

FYM increases both Zn and Cd absorption/mobilization with the passage of time in plants particularly at high doses (Gondek 2010). The concentrations of Cd and Zn were slightly increased due to FYM amendments, which could be attributed to their high inherent concentrations in FYM compared with ACP and ACG (Table 1). In the

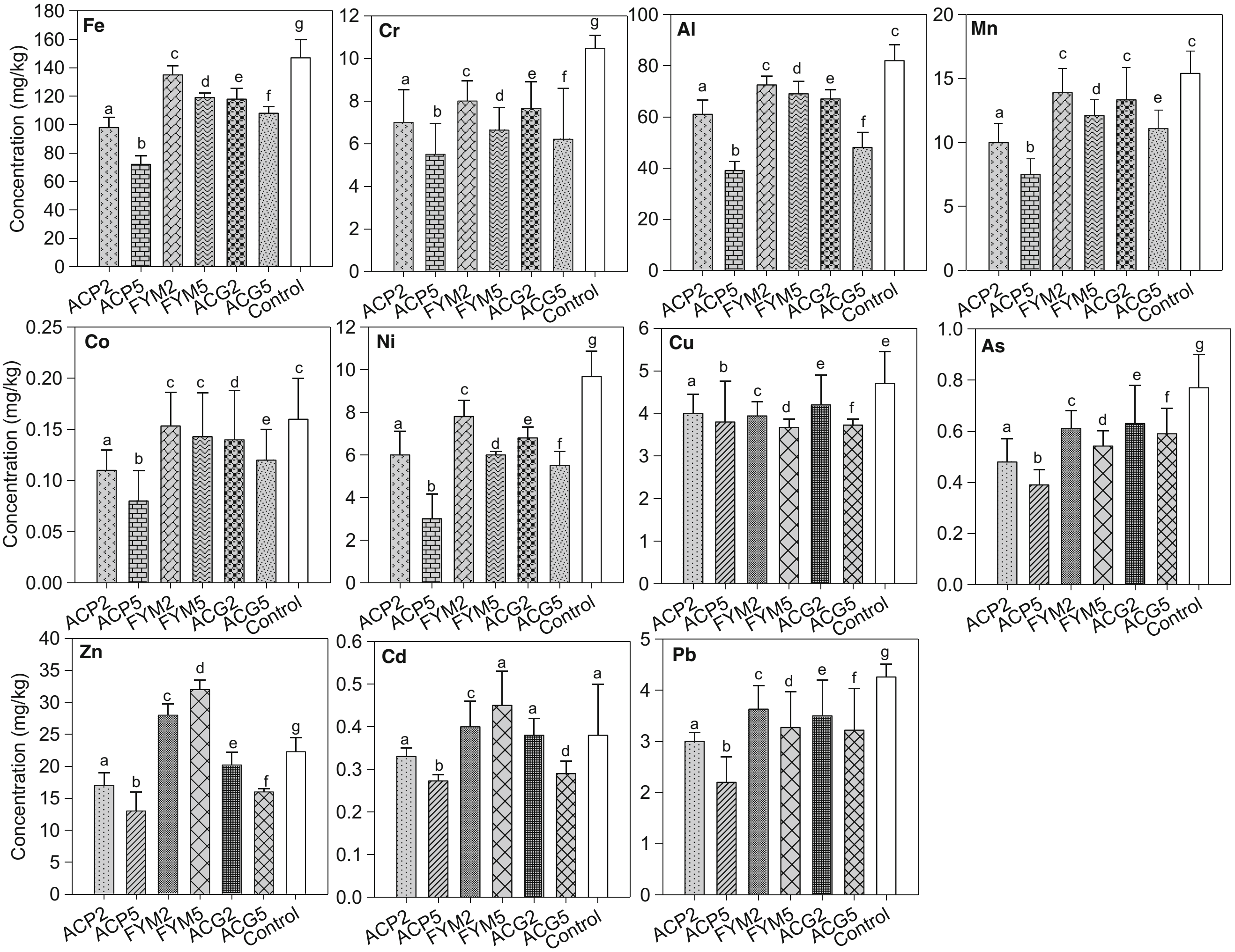

Fig. 2 Bioaccumulation of heavy metal(loid)s in *P. americanum* cultivated in soil amended with ACP, ACG, and FYM (2 and 5 %). *Error bars* represent standard deviation. Similar *letters* indicate no significant difference ($P \leq 0.01$), while different *letters* indicate significant differences compared with the control experiment

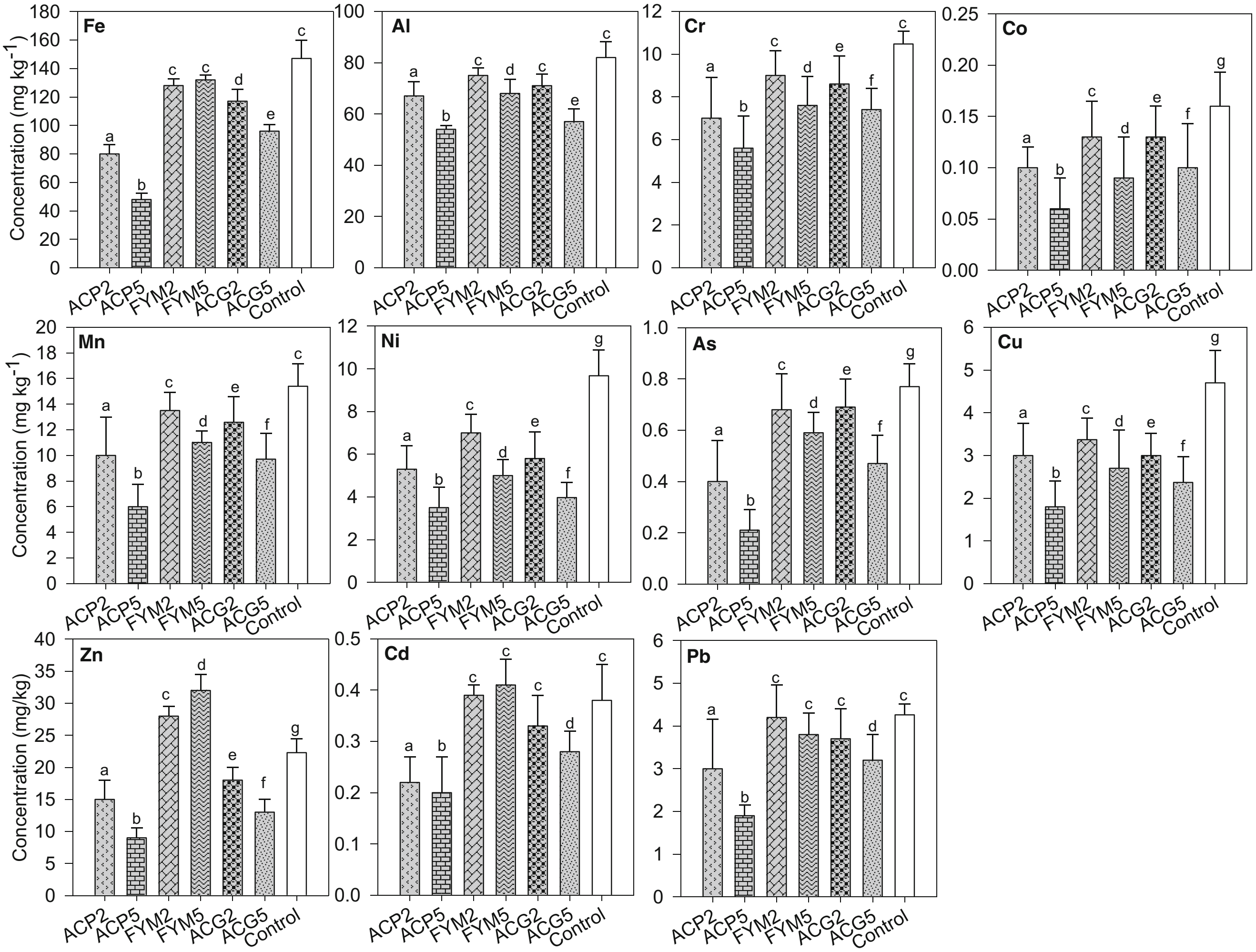

Fig. 3 Bioaccumulation of heavy metal(loid)s in *S. bicolor* cultivated in soil amended with ACP, ACG, and FYM (2 and 5 %). *Error bars* represent standard deviation. Similar *letters* indicate no significant difference ($P \leq 0.01$), while different *letters* indicate significant differences compared with the control experiments

shoots of *P. americanum* and *S. bicolor*, significant decreases were observed in heavy metal(loid) bioaccumulation for the ACP2, ACP5, ACG2, and ACG5 treatments. In all samples, the concentrations of heavy metal(loid)s were reduced in plants grown in amended soils compared with the control. However, the difference in heavy metal(loid) reduction was not significant between the treatments of the same type of AC. ACP was more effective in metal reduction than ACG (2 and 5 %). In plant shoots, the effectiveness of ACG in decreasing heavy metal(loid)s was due to the effect of growth dilution (Allard et al. 2005). In ACG-amended pots, the growth of plants was better than in the ACP treatments, which led to higher biomass production. ACP treatments were highly efficient in reducing metal bioaccumulation in plants compared with other amendments (such as ACG, FYM) and the control because of reduced concentrations of bioavailable metals in these treatments (Table 2) and soil aeration. The changes in soil pH, EC, and other basic properties could be the reason for the reduced bioaccumulation of heavy metal(loid)s in the shoots of plants grown in amended soils (Chamon et al. 2005; Gao and Collins 2009).

Organic matter decomposition limits metal mobility and releases carbonates, phosphates, and other salts, which leads to the formation of insoluble metal complexes (Walker et al. 2003; Kabata and Pendias 2001). FYM or other organic amendments enhance soil organic matter, which increases the metal's binding capacity and reduces their mobility in the soil (Liu et al. 2007). The addition of organic amendments offers several specific and non-specific metal binding sites where desorption is not easy (Shuman 1999). The organic amendments in soil may reduce the bioavailability of heavy metal(loid)s by converting available fractions into non-available fractions, or fractions in combination with carbonates, organic matter, and metal oxides (Walker et al. 2004). This research suggests that, through the adsorption reaction of organic amendments, metals are immobilized. This result could be due to the enhancement of surface charge (Clark et al. 2007) and the availability of metal binding compounds (Gondar and Bernal 2009; Waqas et al. 2015).

Conclusion

The results of this study indicated that almost all organic amendments (ACP2, ACP5, ACG2, ACG5, FYM2, and FYM5) significantly reduced the availability of heavy metal(loid) concentrations in soil and their bioaccumulation in *P. americanum* and *S. bicolor*. The biomasses of these plants significantly ($P \leq 0.01$) decreased with the application of ACP2, ACP5, ACG2, and ACG5, while the biomasses increased with application of FYM2 and FYM5. The heavy metal(loid) concentrations in *P. americanum* and *S. bicolor* shoots significantly ($P \leq 0.01$) decreased (except Cd and Zn) for all amendments. The addition of ACP significantly ($P \leq 0.01$) reduced the heavy metal(loid) concentrations in *P. americanum* and *S. bicolor* but negatively affected the plant growth in ACP-amended mine-impacted soil. ACG and FYM amendments were slightly less effective in reducing bioavailability of heavy metal(loid) concentrations in soil and their bioaccumulation in plants compared with ACP. Furthermore, long-term field research is needed to generalize these results to a broader variety of mine-impacted soil and plants.

Acknowledgments This research work was financially supported by the Higher Education Commission (HEC), Islamabad, Pakistan and University of Peshawar, Pakistan. The authors thank the Institute of Urban Environment, Xiamen China for providing ICP-MS and ICP-OES facilities for metal determination in the extracted samples of organic materials, soil, and plants.

Conflict of interest The authors declare that they have no competing interests.

References

Ahmad M, Lee SS, Yang JE, Ro HM, Lee YH, Ok YS (2012) Effects of soil dilution and amendments (mussel shell, cow bone, and biochar) on Pb availability and phytotoxicity in military shooting range soil. Ecotox Environ Safe 79:225–231

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

Allard AS, Malmberg M, Neilson AH, Remberger M (2005) Accumulation of polycyclic aromatic hydrocarbons from creosote-contaminated soil in selected plants and the oligochaete worm *Enchytraeus crypticus*. J Environ Sci Health 40:2057–2072

Bolan NS, Adriano DC, Naidu R (2003a) Role of phosphorus in immobilization and bioavailability of heavy metals in the soil-plant system. Springer, New York, pp 1–44

Bolan NS, Adriano DC, Natesan R, Koo BJ (2003b) Effects of organic amendments on the reduction and phytoavailability of chromate in mineral soil. J Environ Qual 32:120–128

Bolan N, Kunhikrishnan A, Thangarajan R, Kumpiene J, Park J et al (2014) Remediation of heavy metal(loid)s contaminated soils—to mobilize or to immobilize? J Hazard Mater 266:141–166

Brändli RC, Hartnik T, Henriksen T, Cornelissen G (2008) Sorption of native polyaromatic hydrocarbons (PAH) to black carbon and amended activated carbon in soil. Chemosphere 73:1805–1810

Cala V, Cases MA, Walter I (2005) Biomass production and heavy metal content of *Rosemarinus officinalis* grown on organic waste-amended soil. J Arid Environ 62:401–412

Cao X, Ma LQ (2004) Effects of compost and phosphate on arsenic accumulation from soils near pressure-treated wood. Environ Pollut 132:435–442

Cao X, Ma LQ, Shiralipour A (2003) Effects of compost and phosphate amendments on arsenic mobility in soils and arsenic uptake by the hyper accumulator, *Pteris vittata* L. Environ Pollut 126:157–167

Castaldi P, Santona L, Melis P (2005) Heavy metal immobilisation by chemical amendments in a polluted soil and influence on white lupin growth. Chemosphere 60:365–371

Chamon AS, Gerzabek MH, Mondol MN, Ullah SM, Rahman M, Blum WEH (2005) Influence of soil amendments on heavy metal accumulation in crops on polluted soils of Bangladesh. Commun Soil Sci Plan 36:907–927

Chanpiwat P, Sthiannopkao S, Kim KW (2010) Metal content variation in wastewater and biosludge from Bangkok's central wastewater treatment plants. Microchem J 95:326–332

Cheng Y, Ma RL, Jiao YS, Qiao N, Li TT (2013) Impact of genotype, plant growth regulators and activated charcoal on embryogenesis induction in microspore culture of pepper (*Capsicum annuum* L). S Afr J Bot 88:306–309

Clark GJ, Dodgshun N, Sale PWG, Tang C (2007) Changes in chemical and biological properties of a sodic clay subsoil with addition of organic amendments. Soil Biol Biochem 39:2806–2817

Clemente R, Paredes C, Bernal MP (2007) A field experiment investigating the effects of olive husk and cow manure on heavy metal availability in a contaminated calcareous soil from Murcia (Spain). Agr Ecosyst Environ 118:319–326

Davis JG, Wilson CR (2005) Colorado State University Cooperative Extension-Horticulture.

de Lima LS, Quináia SP, Melquiades FL, de Biasi GE, Garcia JR (2014) Characterization of activated carbons from different sources and the simultaneous adsorption of Cu, Cr, and Zn from metallurgic effluent. Sep Purif Technol 122:421–430

Dobran S, Zagury GJ (2006) Arsenic speciation and mobilization in CCA-contaminated soils: influence of organic matter content. Sci Total Environ 364:239–250

Gao Y, Collins CD (2009) Uptake pathways of polycyclic aromatic hydrocarbons in white clover. Environ Sci Technol 43:6190–6195

Glaser B, Lehmann J, Zech W (2002) Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal—a review. Biol Fert Soils 35:219–230

Gondar D, Bernal MP (2009) Copper binding by olive mill solid waste and its organic matter fractions. Geoderma 149:272–279

Gondek K (2010) Zinc and cadmium accumulation in maize (*Zea mays* L) and the concentration of mobile forms of these metals in soil after application of farmyard manure and sewage sludge. J Elementol 15: 639–652

Gupta S, Nayek S, Saha RH, Satpati S (2008) Assessment of heavy metal accumulation in macrophyte, agricultural soil and crop plants adjacent to discharge zone of sponge iron factory. Environ Geol 55:731–739

Jakob L, Hartnik T, Henriksen T, Elmquist M, Brändli RC, Hale SE, Cornelissen G (2012) PAH-sequestration capacity of granular and powder activated carbon amendments in soil, and their effects on earthworms and plants. Chemosphere 88:699–705

Kabata-Pendias A, Pendias H (2001) Trace elements in soils and plants. CRC Press, London

Khan S, Chao C, Waqas M, Arp HPH, Zhu YG (2013) Sewage sludge biochar influence upon rice (*Oryza sativa* L) yield, metal bioaccumulation and greenhouse gas emissions from acidic paddy soil. Environ Sci Technol 47:8624–8632

Khan S, Waqas M, Ding F, Shamshad I, Arp HPH, Li G (2015) The influence of various biochars on the bioaccessibility and bioaccumulation of PAHs and potentially toxic elements to turnips (*Brassica rapa* L). J Hazard Mater 300:243–253

Lima IM, Marshall WE (2005) Adsorption of selected environmentally important metals by poultry manure-based granular activated carbons. J Chem Technol Biot 80:1054–1061

Liu J, Qian M, Cai G, Zhu Q, Wong MH (2007) Variations between rice cultivars in root secretion of organic acids and the relationship with plant cadmium uptake. Environ Geochem Hlth 29:189–195

Liu L, Chen H, Cai P, Liang W, Huang Q (2009) Immobilization and phytotoxicity of Cd in contaminated soil amended with chicken manure compost. J Hazard Mater 163:563–567

Liu ZT, Zhang GY, Hu ZS (2012) Immobilization of cadmium and lead in contaminated soils by different amendments. Adv Mater Process 415:1662–1666

Lyubchik SB, Lyubchik AI, Lygina ES, Lyubchik SI, Makarova TL et al (2008) Simultaneous removal of 3d transition metals from multicomponent solutions by activated carbons from co-mingled wastes. Sep Purif Technol 60:264–271

McGowen SL, Basta NT, Brown GO (2001) Use of diammonium phosphate to reduce heavy metal solubility and transport in smelter-contaminated soil. J Environ Qual 30:493–500

Mench M, Lepp N, Bert V, Schwitzguébel JP, Gawronski SW, Schröder P, Vangronsveld J (2010) Successes and limitations of phytotechnologies at field scale: outcomes, assessment and outlook from COST Action 859. J Soil Sediment 10:1039–1070

Modin H, Persson KM, Andersson A, van Praagh M (2011) Removal of metals from landfill leachate by sorption to activated carbon, bone meal and iron fines. J Hazard Mater 189:749–754

Mouta ER, Soares MR, Casagrande JC (2008) Copper adsorption as a function of solution parameters of variable charge soils. J Braz Chem Soc 19:996–1009

Nawab J, Shah MT, Khan S, Qing H, Khan K, Ali R (2015a) Quantification of heavy metals in mining affected soil and their bioaccumulation in native plant species. Int J Phytoremediat 17: 801–813

Nawab J, Khan S, Shah MT, Qamar Z, Din I, Mahmood Q, Gul N, Qing H (2015b) Contamination of soil, medicinal, and fodder plants with lead and cadmium present in mine-affected areas, Northern Pakistan. J Environ Monitor 187:605

Nwachukwu OI, Pulford ID (2009) Soil metal immobilization and ryegrass uptake of lead, copper and zinc as affected by application of organic materials as soil amendments in a short-term greenhouse trial. Soil Use Manage 25:159–167

Ok YS, Oh SE, Ahmad M, Hyun S, Kim KR, Moon DH et al (2010) Effects of natural and calcined oyster shells on Cd and Pb immobilization in contaminated soils. Environ Earth Sci 61:1301–1308

Rate AW, Lee KM, French PA (2004) Application of biosolids in mineral sands rehabilitation: use of stockpiled topsoil decrease trace elements by plants. Bioresource Technol 3:223–231

Rhodes AH, Carlin A, Semple KT (2008) Impact of black carbon in the extraction and mineralization of phenanthrene in soil. Environ Sci Technol 42:740–745

Ryan J, Estefan G, Rashid (2001) A Soil and plant analysis laboratory manual, Interaction Center for Agricultural Research in the Dry Areas (ICARDA), Aleppo, Syria, 2nd ed, p. 172.

SEPA (1995) Environmental quality standard for soils. State Environmental Protection Administration, China

Shuman LM (1999) Organic waste amendments effect on zinc fractions of two soils. J Environ Qual 28:1442–1447

Stewart BA, Robinson CA, Parker DB (2000) Examples and case studies of beneficial reuse of beef cattle byproducts. In: Dick WA (ed) Land application of agricultural, industrial, and municipal by-products. Soil Sci Soc Am J Inc, Madison, Wisconsin

Tomaszewski JE, Werner D, Luthy RG (2007) Activated carbon amendment as a treatment for residual DDT in sediment from a superfund site in San Francisco Bay, Richmond, California, USA. Environ Toxicol Chem 26:2143–2150

Ucer A, Uyanik A, Aygun F (2006) Adsorption of Cu (II), Cd (II), Zn (II), Mn (II), and Fe (III) ions by tannic acid immobilized activated carbon. Sep Purif Technol 47:113–118

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

Walker DJ, Clemente R, Roig A, Bernal MP (2003) The effects of soil amendments on heavy metal bioavailability in two contaminated Mediterranean soils. Environ Pollut 122:303–312

Walker DJ, Clemente R, Bernal MP (2004) Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of *Chenopodium album* L. in a soil contaminated by pyritic mine waste. Chemosphere 57:215–224

Waqas M, Khan S, Qing H, Ried BJ, Chai C (2014) The effects of sewage sludge and sewage sludge biochar on PAHs and potentially toxic element bioaccumulation in *Cucumis sativa* L. Chemosphere 105: 53–61

Waqas M, Li G, Khan S, Shamshad I, Reid B J, Qamar Z, Chao C (2015) Application of sewage sludge and sewage sludge biochar to reduce polycyclic aromatic hydrocarbons (PAH) and potentially toxic elements (PTE) accumulation in tomato. Environ Sci Pollut Res DOI 10.1007/s11356-015-4432-8.

Wei B, Yang L (2010) Heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. A review. Microchem J 94:99–107

Williamson A, Johnson MS (1981) Reclamation of metalliferous mine wastes. Effect of heavy metal pollution on plants. Springer, Netherlands

Zeng F, Ali S, Zhang H, Ouyang Y, Qiu B, Wu F, Zhang G (2011) The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants. Environ Pollut 159:84–91

Zimmerman JR, Ghosh U, Millward RN, Bridges TS, Luthy RG (2004) Addition of carbon sorbents to reduce PCB and PAH bioavailability in marine sediments: physicochemical tests. Environ Sci Technol 38:5458–5464