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RESEARCH ARTICLE

Effects of amendments and aided phytostabilization of an energy crop on the metal availability and leaching in mine tailings using a pot test

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Abstract

A complete orthogonal experiment using a pot test is conducted to investigate the effects of four amendments (biochar, peat, manure, and non-contaminated soil (NCS)) on the metal availability, mobility, and phytostabilization potential of an energy crop, king grass (*Pennisetum purpureum* × *P. thyphoideum*), in Pb/Zn mine tailings. The addition of amendments significantly increased the pH and fertility of the tailings, while significantly decreasing the heavy metal available contents in the tailings. The available Cd, Pb, Zn, and As concentrations in the tailings in the treatment amended with biochar+NCS+peat+manure were 51.00%, 36.62%, 50.57%, and 75.88%, respectively, lower than those in the treatment control. The king grass survived in the tailings without amendments, while amendments made the plant grow well or better in the tailings than in NCS. The addition of amendments significantly reduced the content of heavy metals and bioaccumulation factor (BCF) in the plant root but increased the translocation factor (TF) of Cd, Zn, and As and had little effect on the TF of Pb. The TF for heavy metals in plant were lower than one for all of the treatments. During a leaching period of 30 days, the pH of the leachate declined slowly and then maintained at 6.0~6.6. The addition of the amendments significantly reduced the metal concentrations of the leachates, and the highest declines were 50.46%, 20.04%, 41.58%, and 47.04% for Cd, Pb, Zn, and As, respectively. Biochar had a higher immobilization capacity for Cd, Pb, Zn, and As than manure, peat, and NCS. King grass could be used to aid phytostabilization for Cd- and Pb-polluted tailings, and biochar-rich amendments were effective for the in situ immobilization of metals. Further field monitoring is necessary to demonstrate the effectiveness of king grass and amendments under the climatic conditions of China.

Keywords Mine tailings · Amendment · Phytostabilization · Heavy metal · Leachate

Introduction

Mine tailings are a legacy of ore beneficiation. Large amounts of tailings are produced during the process of mining (Cousins et al. 2009; Li and Huang 2015). Mine tailings are long-term sources of environmental pollution that pose a high risk to human health as they contain high levels of heavy metals and are susceptible to wind dispersal and water erosion (Lee et al. 2014). There is a pressing need to remediate mine tailings to reduce the migration of tailings and heavy metal leaching.

Phytostabilization is a cost-effective remediation technique that is often used for barren contaminated area recovery, especially for mine tailings. This technique can stabilize contaminants in mediums and protect barren contaminated areas by accumulating or precipitating metals in plant roots or the root zone (Elouear et al. 2014; Galende et al. 2014). Energy crops are being utilized as an appropriate plant species for a new alternative method for phytostabilization. Their use is beneficial because cultivating them in metal-contaminated lands can achieve both the objective of land remediation and biomass production (Weyens et al. 2009; Zhang et al. 2014).

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King grass (*Pennisetum purpureum* K. Schumach × *P. thyphoideum* Rich) is an important energy crop used for cellulosic biofuels and electric power plants. It has been reported that this plant has suitable characteristics for use in phytoremediation of soils contaminated with Cd, Pb, Zn, As, and Ni (Zhang et al. 2014, 2017a, b). However, whether this species has phytoremediation potential for tailings is unclear.

Furthermore, due to the harsh conditions in the mine tailings, such as extreme pH, high salt content, lack of required nutrients, metal toxicities, and poor water retention, it is very difficult for plants to grow (Lee et al. 2014). Therefore, amendments are needed to aid phytostabilization to improve the living environment of plants and reduce the mobility and leaching of heavy metals. Recently, biochar has been found to be a good remediation amendment for contaminated soils and tailings (Beesley et al. 2011; Beesley and Marmiroli 2011; Forján et al. 2016; Li et al. 2018). However, the remediation effects of different biochar on different heavy metals or tailings are quite different. Some studies have found that biochar made by *Acacia dealbata* can reduce available concentrations of metals, such as Cu, Pb, and Zn, and increase the soil pH (Forján et al. 2016), while other studies have indicated that the addition of biochar made by basswood did not significantly reduce leaching of the primary contaminants (Cu and Ni in acidic tailings and As in alkaline tailings) (Beauchemin et al. 2015). The biochar used in this study was made using *Leersia hexandra* Swartz, which is a hygrophyte that grows extensively as a paddy weed. This biochar has a high biosorption capability for heavy metals from aqueous solutions (Zhang et al. 2017a, b). However, the stability of heavy metals in biochar and their assistance to phytostabilization in tailings have not been reported. Non-contaminated soil, manure, and peat are three common and cheap amendments, and they have been reported to have the abilities to promote plant growth and maximize the stabilization of heavy metals (Houben et al. 2012; Mignardi et al. 2013; Pérez-Esteban et al. 2014). It was found that peat addition significantly reduced the phytoremediation time of Cu-, Mn-, Zn-, and B-contaminated soils and Pb-, Cd-, and Zn-contaminated soils compared with treatment with no peat addition (Pichtel and Bradway 2008; Abreu et al. 2012). Manure could significantly increase plant growth and nutrition and decrease concentrations of available Cd, Pb, Zn, and Cu in soils (Pichtel and Bradway 2008; Zhang et al. 2016). In addition, the interaction effects of biochar, soil, manure, and peat on tailings have not been studied so far. Whether these four amendments could aid the phytostabilization of lead-zinc mine tailings using king grass is unclear.

The leaching of heavy metals in tailings is an important index to evaluate the impact of tailings on the surrounding environment. Various methods have been used to reduce the leaching rate of heavy metals in tailings to reduce the risk to the surrounding environment (Schwab et al. 2007; Lee et al. 2014). After phytostabilization (harvesting of plants), the total amount and fractions of heavy metals in tailings would change, which may affect the leaching of heavy metals in tailings (Sheoran et al. 2011; Ali et al. 2013). However, there are few reports on the leaching of heavy metals in tailings with amendments after phytostabilization (harvesting of plants). Therefore, the aim of this study is to investigate the effects of four amendments (non-contaminated soil, biochar, manure, and peat) on the immobilization of metals. The phytostabilization capacity of king grass on lead and zinc tailings is also investigated.

Materials and methods

Materials

The stem nodes of king grass were purchased from the Jiangxi Scarecrow Agricultural Garden Company, China, and then used for the pot experiment. Tailings were collected from the lead-zinc ore mining district (Huanjiang County of Hechi City, Guangxi Province, China) and then air-dried and sieved through a 0.85-mm mesh. The top layer (20 cm) of non-contaminated soil was collected from a farmland located in Guilin, China. Tailings and non-contaminated soil were used in the following experiments, and their properties are shown in Table 1. Pig manure with a pH of 8.95 and organic matter content of 4.46% was obtained from a local farmer in Guilin City, China. Peat was obtained from a flower market in Guilin City, China, with a pH of 6.87 and organic matter content of 2.71%. Biochar was made according to Zhang et al. (2017a, b) and found to have properties of a 7.54 pH and organic matter content of 34.03%.

Experimental design

Pot experiment

The experiment was conducted at Guilin, China. Seventeen treatments were constructed, and they are shown in Table 2. There were three replicates of each treatment. Two kilograms of air-dried tailings was placed in each plastic pot having a diameter of 20 cm and a height of 15 cm. After that, amendments were added to the pots according to the application rates in Table 2. Then, two individual stem nodes of king grass were rooted into the tailings in each pot. The plants were watered daily to keep the moisture of the tailings at 70~80%. Sixty days later, the heights of the plants were measured. Then, the plant shoots were cut using scissors and the roots were dug up. After this, the plants were cleaned up with tap water and deionized water. Then, the plants were dried to a constant mass, ground, and stored for analysis. Tailings in the pots after

Table 1 Properties of the polluted tailings and non-contaminated soil in the pot test

Parameters	Polluted tailings*	Non-contaminated soil*	The threshold values required for farmland of China (Office of National Soil Survey 1997; National Standardization Committee 1995)
pH	7.963 ± 0.030	7.890 ± 0.020	7.50
Organic matter (%)	1.309 ± 0.088	2.267 ± 0.030	2.00
Eh	207.00 ± 1.155	220.00 ± 1.528	/
Total N (g kg^{-1})	0.033 ± 0.033	0.633 ± 0.033	1.00
Total P (g kg^{-1})	0.034 ± 0.005	1.130 ± 0.005	1.20
Total K (g kg^{-1})	1.030 ± 0.019	56.766 ± 1.050	18.00
Total Cd concentrations (mg kg^{-1})	30.94 ± 1.79	ND	1.00
Total Pb concentrations (mg kg^{-1})	813.70 ± 100.06	32.63 ± 6.10	350.00
Total Zn concentrations (mg kg^{-1})	3975.37 ± 517.85	172.55 ± 19.33	300.00
Total As concentrations (mg kg^{-1})	24.96 ± 1.72	10.91 ± 0.48	25.00

*Mean ± S.E.; *n* = 3; ND means the value lower than the detection value

the plants were grown were collected and used for sample analysis and the following column experiment.

Column experiment

To investigate the impacts of the amendments and plants on heavy metal leaching from the tailings of 17 treatments, a leaching experiment was conducted using the tailings after the plants were grown in these treatments. Each column was made of a PVC pipe with a 15-cm diameter and 30-cm length. Mine tailings collected from the above pot experiments after the plants were grown were added in each column to a depth of 20 cm. To remove for the plant effects, the unused tailings were used for leaching, namely CK0 (Table 2). The leaching solution was prepared using nitric acid and sulfuric acid (the molar concentration of SO_4^{2-} and NO_3^- was 1:1) to adjust the pH to 5.5 ± 0.2 based on local precipitation data of Huanjiang City, Guangxi Province. This solution was then introduced to the top of the columns continuously, and the leaching rate was controlled at 50 mL per day using a water pump and an air valve. Leachate was collected continuously from the bottom of each column for 1 month using polyethylene sample bottles, and the sample bottles were changed every 3 days. The experiment was run day and night without intermittent operation. Then, the leachate was passed through 0.22-μm polycarbonate membranes to remove large particles and soil microbes, and the resulting leachate was used for further analysis.

Sample and statistical analysis

The properties of the tailings and amendments were determined on the basis of Liu (1996). The pH of the pig manure, peat, non-contaminated soil, and tailing samples (solid:distilled water = 1:2.5) were measured using a pH meter (UB-7, Denver Instruments (Beijing) Co., Ltd., China). The organic matter of the pig manure, peat, non-contaminated soil, and tailing samples was determined by the potassium dichromate oxidation method using spectrophotometry (V-5800PC, Shanghai Metash Instruments Co., Ltd., China). Total nitrogen was determined using an elemental analyzer (EA2400 II, Platinum Elmer Instruments Co., Ltd., USA). Total phosphorus was determined by the sulfuric acid-perchloric acid digestion method using spectrophotometry (V-5800PC, Shanghai Metash Instruments Co., Ltd., China). The Eh of the tailings was determined using the direct insertion of a redox potentiometer (FJA-5, Nanjing Dropping Instrument Equipment Co., Ltd., China).

The total concentration of metals in the tailings and plants was digested by concentrated HNO_3 and H_2O_2 with volume proportions of 5:1 using the method recommended by the US Environmental Protection Agency (USEPA method 3052). The available concentration of metal in the tailings was extracted using 0.1 mol L^{-1} HCl according to the method of

Table 2 Experimental treatments in the pot test

Treatments	Amendments*
NCS	Non-contaminated soil (NCS)
CK0	Unused tailings
CK	Tailings without amendments
B	Tailings with 0.4% biochar
S	Tailings with 10% NCS
P	Tailings with 2% peat
M	Tailings with 1% manure
B+S	Tailings with 0.2% biochar+5% NCS
B+P	Tailings with 0.2% biochar+1% peat
B+M	Tailings with 0.2% biochar+0.5% manure
S+P	Tailings with 5% NCS+1% peat
P+M	Tailings with 1% peat+0.5% manure
S+M	Tailings with 5% NCS+0.5% manure
B+S+P	Tailings with 0.13% biochar+3.3% NCS+0.67% peat
B+S+M	Tailings with 0.13% biochar+3.3% NCS+0.33% manure
B+P+M	Tailings with 0.13% biochar+0.67% peat+0.33% manure
S+P+M	Tailings with 3.3% NCS+0.67% peat+0.33% manure
B+S+P+M	Tailings with 0.1% biochar+2.5% NCS+0.5% peat+0.25% manure

*The additive amount is the percentage of the tailing mass

Baker and Amacher (1982). Leachate samples were digested using concentrated HNO_3 and concentrated $HClO_4$ with volume proportions of 5:1. The concentrations of Cd, Pb, Zn, and K of all of the samples were measured using an inductively coupled plasma atomic emission spectrometer (ICP, Optima 7000DV, Company of PerkinElmer, USA). The concentrations of As of all of the samples were determined using an atomic fluorescence spectrophotometer (AFS, AFS-933, Company of Jitian, China).

The bioaccumulation factor (BCF), the ratio between the root, stem, or leaf to soil concentrations, and a translocation factor (TF), the ratio of metal concentration of a plant stem or leaf to those of the plant root, were used to assess the phytostabilization efficiency of king grass (Alagić et al. 2018; Tošić et al. 2016). Data were analyzed using Pearson's correlation coefficients and one-way ANOVAs using SPSS 16.0 statistical software.

Results and discussion

Generally, mine tailings have high heavy metal pollution contents and are infertile. In this study, the pH of tailings were in the alkaline range (Table 1). The total N, P, and K of the tailings were lower than the very insufficient class of soil nutrient standard in China (0.50, 0.40, and 6.00 g kg^{-1}). The organic matter was lower than the insufficient class of soil nutrient standard in China (2.00 mg kg^{-1}). The concentrations of total Cd, Pb, and Zn in the tailings were 30.94, 2.32, and 13.25 times higher than the threshold values required for farmland in China (National Standardization Committee 1995), respectively. However, the concentration of total As was closer the threshold values required for farmlands of China. These results indicated that the tailings collected from the lead-zinc mining district in China were alkaline, seriously polluted by Cd, Pb, and Zn, and had low contents of N, P, and K.

It is well known that because the tailings are toxic and infertile, plants have difficulty growing in such environment (Park et al. 2011a; Gil-Loaiza et al. 2016). Therefore, amendments are needed to improve the properties of tailings and affect the existing form of heavy metals in tailings (Houben et al. 2012). The properties and availabilities of Cd, Pb, Zn, and As concentrations for amended tailings are shown in Figs. 1 and 2. The pH ranged from 7.77 (treatment P+M) to 8.33 (treatment B+S), and the organic matter content ranged from 1.31 (treatment CK (tailings without amendments)) to 2.42% (treatment B+P+M). The total N, P, and K concentrations of the amended tailings were 0.033~0.633, 0.034~1.130, and 1.030~56.766 mg kg^{-1}, respectively. The available Cd, Zn, and As concentrations were highest in treatment CK (8.16, 791.48, and 2.30 mg kg^{-1}, respectively) and lowest in treatment B+S+P+M (4.00, 391.26, and 0.55 mg kg^{-1}, respectively). The available Pb concentrations were highest in treatment P (162.44 mg kg^{-1}), followed by treatment CK (148.68 mg kg^{-1}), and lowest in treatment B+S+P+M (94.23 mg kg^{-1}). However, there was no significant difference in the available Pb concentrations between treatment P and treatment CK ($p > 0.05$). The available Cd, Pb, Zn, and As

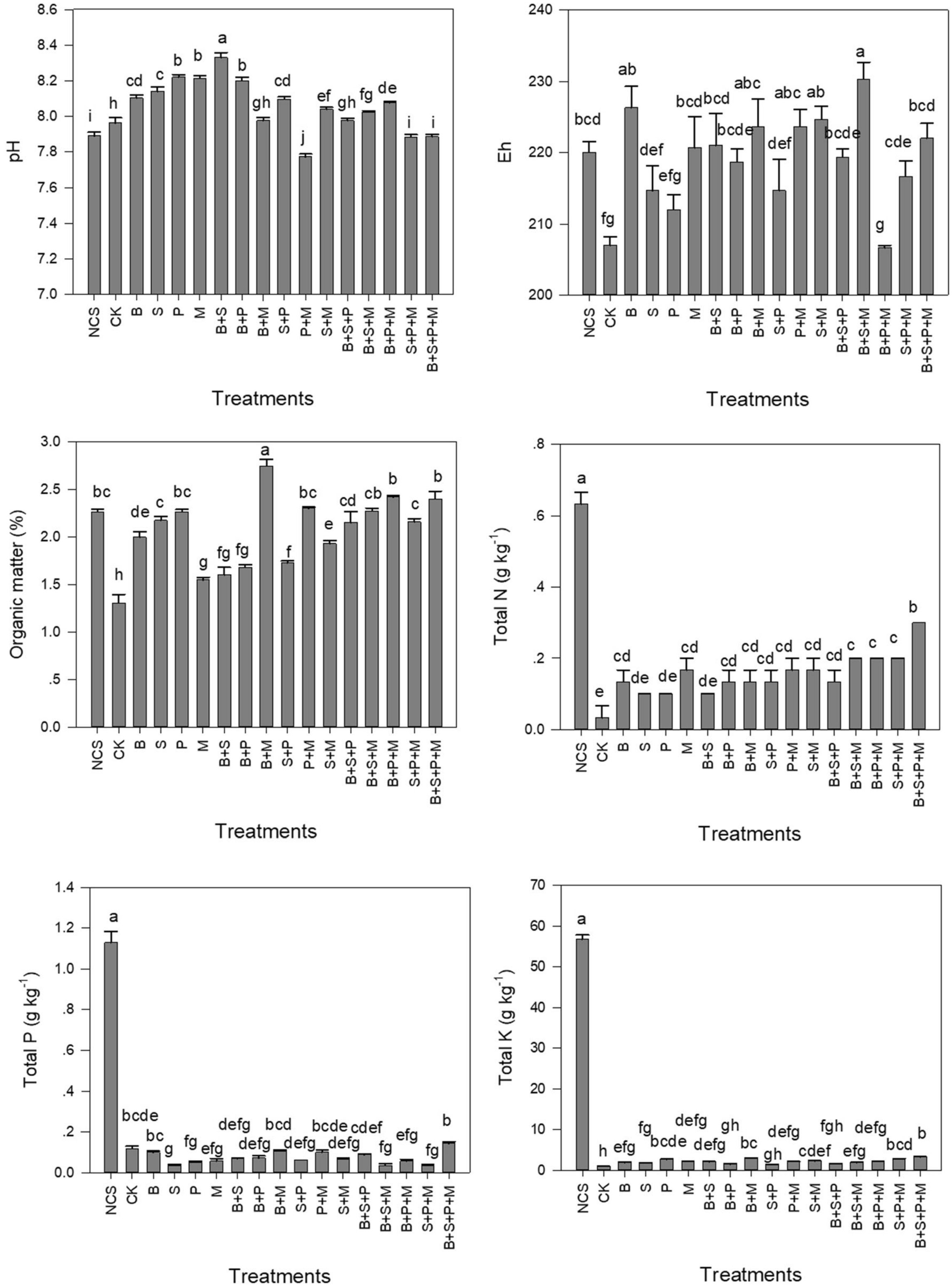

Fig. 1 Amended tailing properties from experiment 1 of the pot test. The values represent the mean ± S.E., $n = 3$. Different letters indicate significant differences between the means (LSD test, $p \leq 0.05$)

concentrations of tailings in treatment B+S+P+M were 51.00%, 36.62%, 50.57%, and 75.88%, respectively, lower than those in the CK treatment. The results showed that the amendments improved soil nutrient conditions and pH but reduced the available Cd, Pb, Zn, and As concentrations in the tailings.

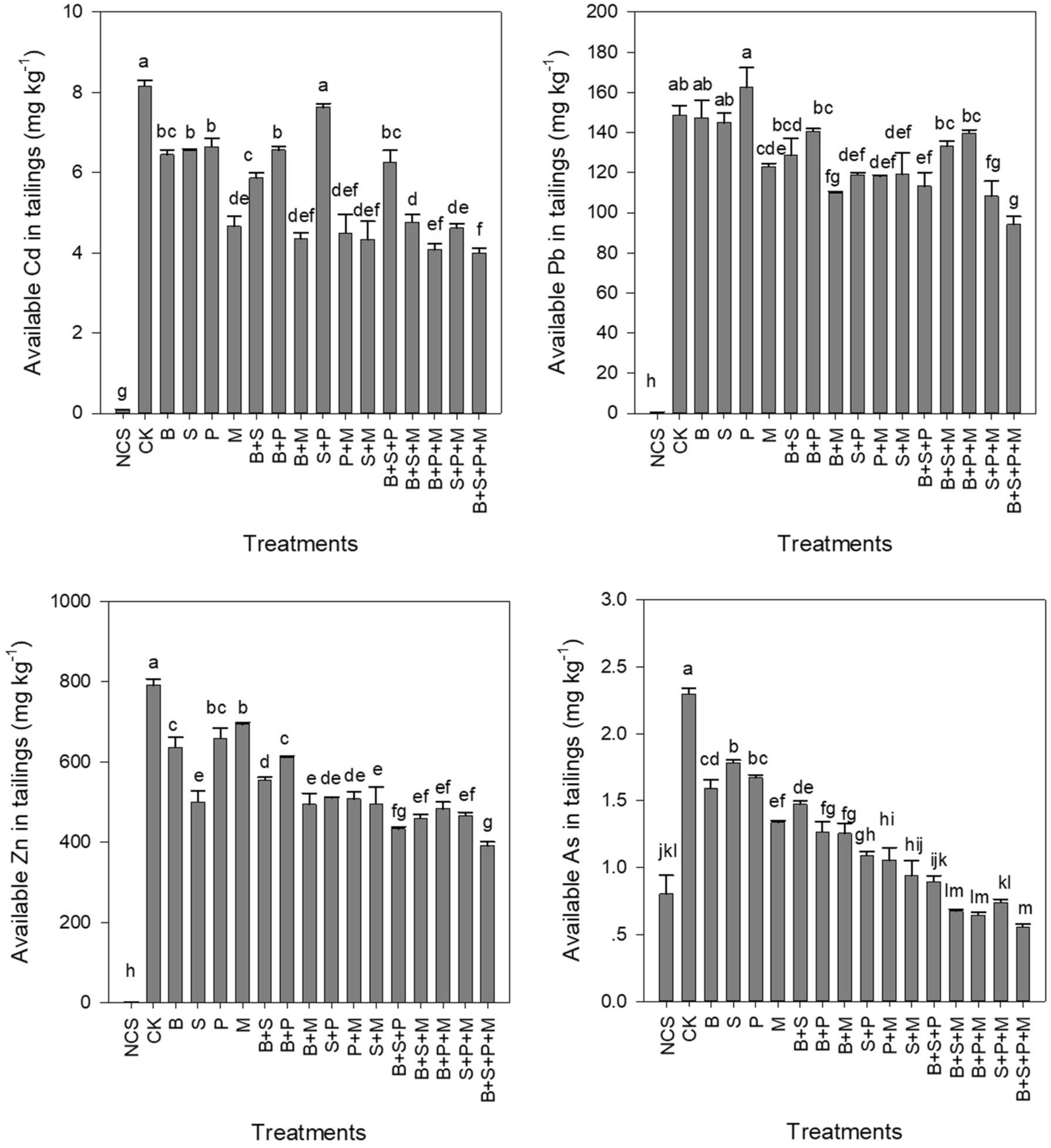

Fig. 2 Available Cd, Pb, Zn, and As concentrations of the amended tailings in the pot test. The values represent the mean ± S.E., $n = 3$. Different letters indicate significant differences between the means (LSD test, $p \leq 0.05$)

It is well known that the content of available heavy metals in tailings has a negative correlation with pH, because an increase in pH would increase metal sorption onto negative sites or the precipitation of metals in the form of oxides, hydroxides, carbonates, and phosphates (Bradl 2004; Houben et al. 2012). However, the content of available Cd, Pb, Zn, and As in the tailings had a significant positive relationship with pH ($p \leq 0.05$) (Fig. 3), which was in contrast with previous studies (Walker et al. 2004; Bradl 2004). This may have been because the change ranges of pH in those studies were relatively large (from acidic to alkaline), while the pH of tailings in the present study was small (7.7~7.9). Moreover, the available concentrations of Cd, Zn, and As in tailings were negatively correlated with organic matter (Fig. 3), which may have been because the solubility of Cd, Zn, and As depends strongly on the sorption process of organic matter (Park et al. 2011b; Pérez-Esteban et al. 2014).

High tolerance is often used to assess whether the plants are suitable for phytostabilization (Marques et al. 2009). After 60 days of growth, the king grass survived in the tailings and the plant height was 40 cm in the CK treatment. However, the plant height was 124.67 cm in the treatment with B+S+P+M, which had no significant difference with the NCS treatment ($p > 0.05$, Fig. 4). The biomass of king

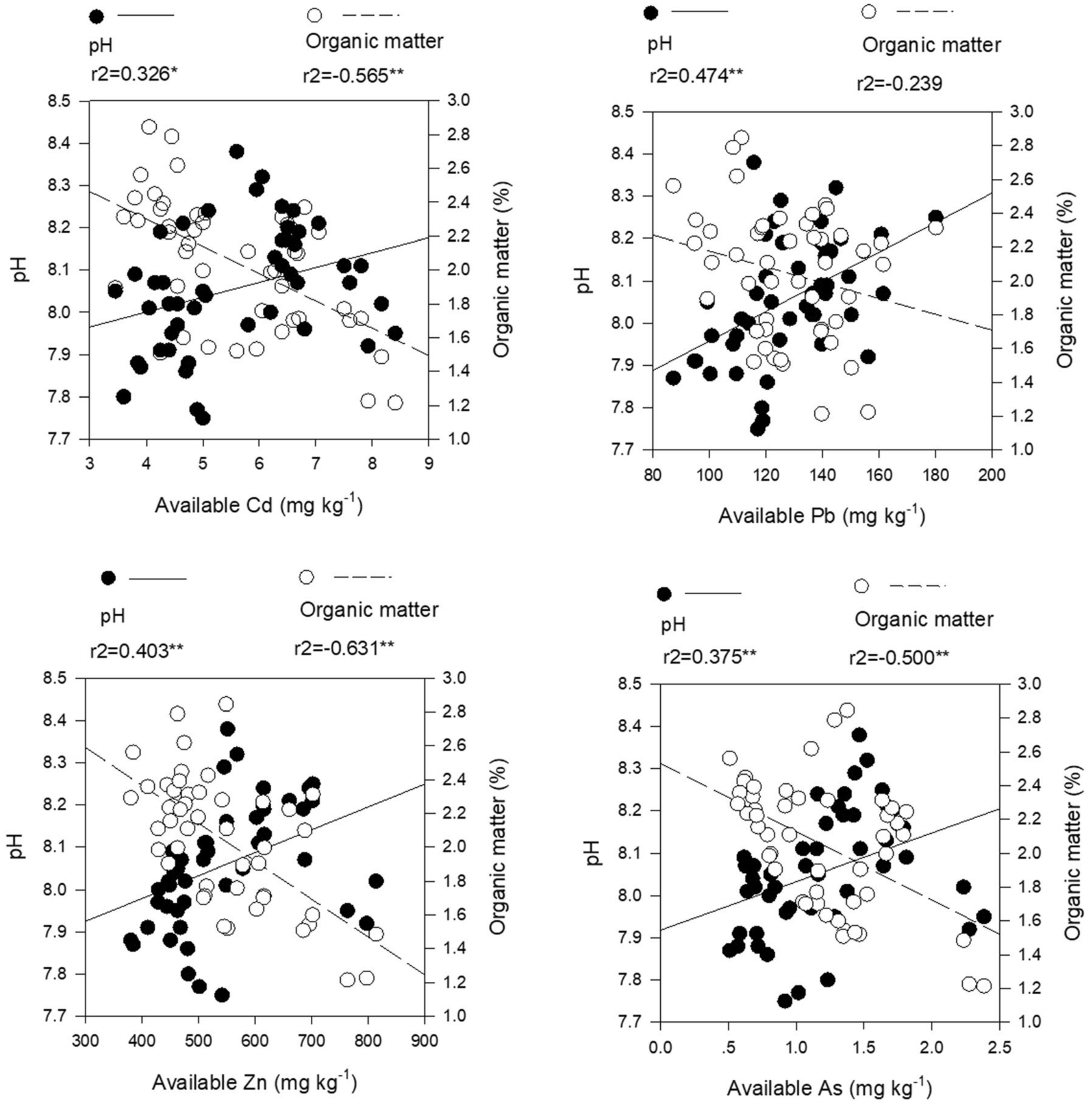

Fig. 3 Pearson correlation analysis between available Cd, Pb, Zn, and As concentrations and pH and organic matter content of tailings in the pot test. *Correlation is significant at the 0.05 level (two-tailed). **Correlation is significant at the 0.01 level (two-tailed)

grass was lowest in the CK treatment and highest in the B+S+P+M treatment. Plant biomass in the B+M, B+S+M, B+P+M, and S+P+M treatments had no significant differences with those in the CS treatment ($p > 0.05$), while the biomass in the B+S+P+M treatment was significantly higher than that in the NCS treatment ($p \leq 0.05$). The fact that the king grass survived in the tailings without amendments indicated that this plant had a high tolerance to the harsh environment of tailings. The addition of amendments of 0.2% biochar+0.5% manure, 0.13% biochar+3.3% NCS+0.33% manure, 0.13% biochar+0.67% peat+0.33% manure, 3.3% NCS+0.67% peat+0.33% manure, or 0.1% biochar+2.5% NCS+0.5% peat+0.25% manure to the tailings significantly improved plant growth and allowed the plants to grow well or better in tailings than in non-contaminated soil ($p \leq 0.05$). This may because the four amendments, i.e., manure, biochar, peat, and non-contaminated soil, which are rich in organic matter, supplied nutrients for the plants, as well as reduced the mobility of the contaminants in the metal-polluted mediums (Xu 2017; Walker et al. 2004; Park et al. 2011a).

Furthermore, a low translocation factor (TF), a low bioaccumulation factor of the shoot (BCF of shoot), and a high bioaccumulation factor of root (BCF of root) represent the most proper indicators of plant usability in phytostabilization, as a phytoremediation method mostly based on metal retention in plant roots (Alagić et al. 2018; Tošić et al. 2016). In comparison with king grass growing in tailings without amendments, the concentrations of Cd, Pb, Zn, and As in the roots were 19.73~89.08, 561.53~1398.99, 572.51~1125.03, and 2.24~8.34 mg kg^{-1}, respectively

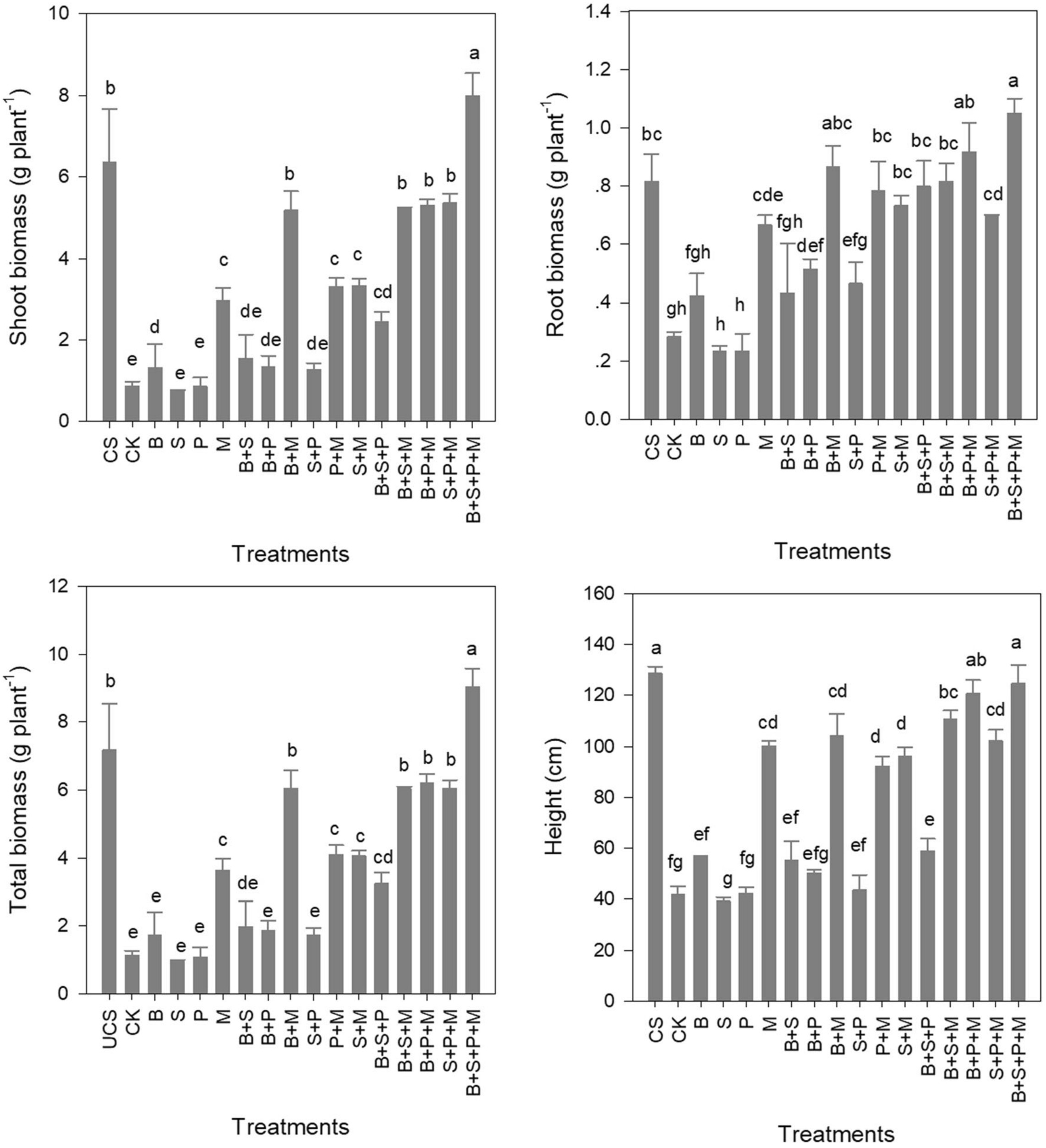

Fig. 4 Growth indicators at the time of harvest in the pot test. The values represent the mean ± S.E., *n* = 3. Different letters indicate significant differences between the means (LSD test, $p \leq 0.05$)

(Fig. 5). The concentrations of Cd, Pb, Zn, and As in the stems were 5.85~47.93, 13.50~47.91, 36.72~502.00, and 0~0.11 mg kg^{-1}, respectively. The concentrations of Cd, Pb, Zn, and As in the leaves were 2.45~14.70, 29.32~63.64, 85.83~177.72, and 0.19~0.79 mg kg^{-1}, respectively. The BCF of Cd, Pb, Zn, and As in the plant stems and leaves were 0.08~0.69, 0.02~0.08, 0.01~0.09, and 0~0.04, respectively, and the BCF of Cd, Pb, Zn, and As in the plant roots were 0.59~1.28, 0.71~1.31, 0.14~0.27, and 0.11~0.22, respectively, in all of the tailing treatments (Fig. 6). These results indicated that king grass had a pretty good stabilizing effect for heavy metals such as Cd, and Pb, whereas in the case of Zn and As, this plant species was not so successful. The addition of the amendments significantly reduced the content and BCF of heavy metals in plant roots in all the tailing treatments. Meanwhile, compared with the control treatment, almost all the amendment treatments significantly decreased or had no significant influence on the BCF of heavy metals in plant stems and leaves, except for the BCF of Cd in plant stems in the treatments with P and B+S, the BCF of Pb in plant stems in the treatments with P and B+P, the BCF of Zn in plant stems in the treatment with P, the BCF of Zn in plant leaves in the treatments with S, B+S+P, and B+P+M, the BCF of As in plant stems in the treatments with B+M and P+M, and the

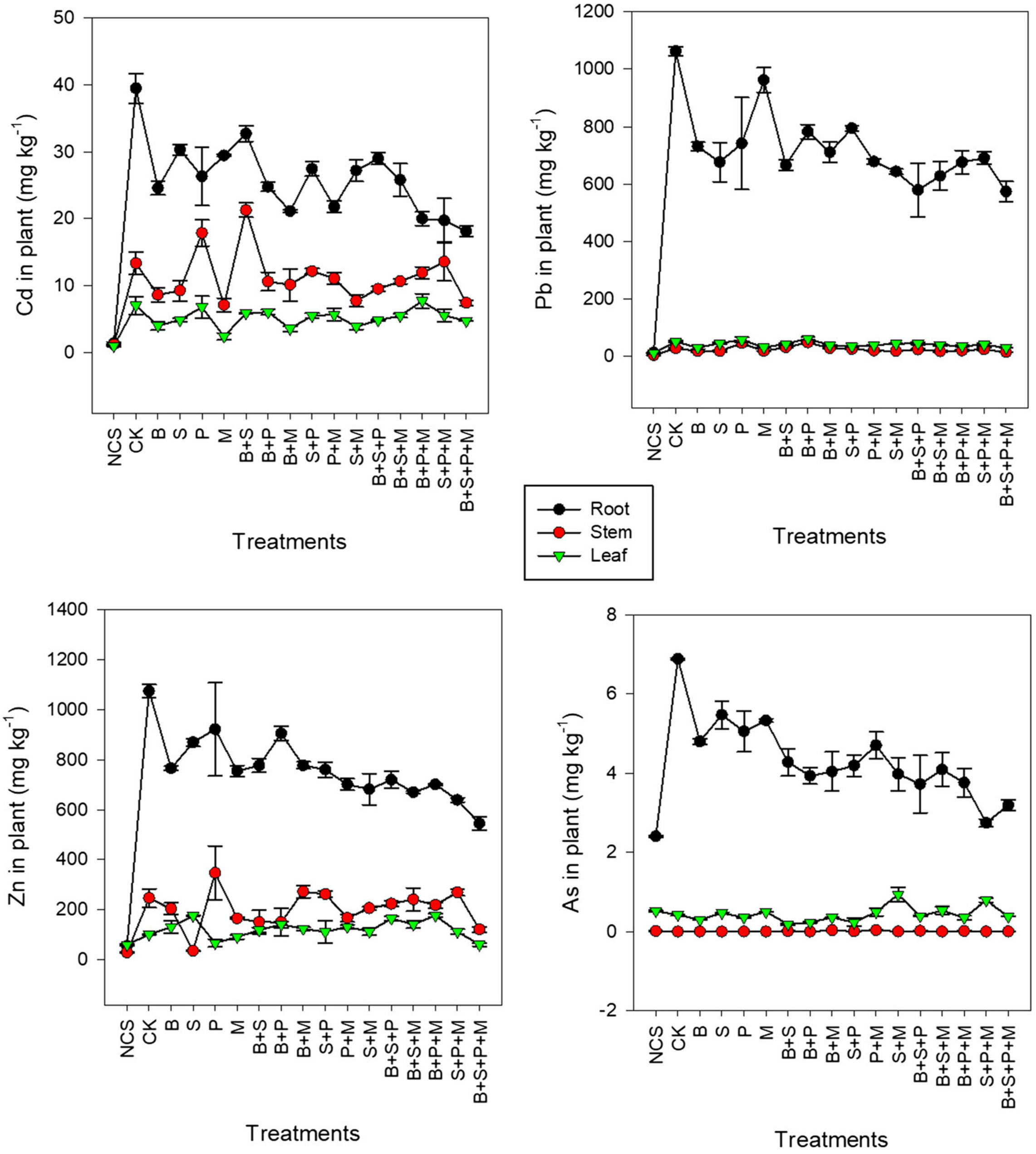

Fig. 5 The metal concentrations of king grass in the pot test. The values represent the mean ± S.E., *n* = 3

BCF of As in plant leaves in the treatments with S+M and S+P+M. The translocation factors (TF) of Cd, Pb, Zn, and As of plant stems and leaves in all of the tailing treatments were less than 1, i.e., 0.08~0.80, 0.02~0.09, 0.04~0.42, and 0~0.29, respectively (Fig. 7). These results indicated that metals were translocated to the stem and leaf from the soil or root in very small quantities. Compared with the control treatment, the amendment treatments with M, S+P, and B+S+P+M had no significant effect on the TF of heavy metal in plant stems and leaves, while other amendment treatments significantly increased or had no significant influence on those TF. Meanwhile, the effect of amendments on the TF of Cd, Zn, and As in plant stems and leaves is greater than that of Pb. These may have been because Cd and Zn are readily bioavailable and Pb is least bioavailable (Prasad 2003; Ali et al. 2013), and As is more bioavailable in a reducing condition (Xu et al. 2008; Norton et al. 2013). The application of amendments may only affect the transport capacity of Cd, Zn, and As in plants by improving plant growth and changing the form of heavy metals in tailings (Marques et al. 2009; Sheoran et al. 2011; Ali et al. 2013). Furthermore, although the BCF of heavy metals in plant stems and leaves were low, the heavy metal contents in plant stems and leaves were still high due to the high concentrations of heavy metal in tailings. Therefore,

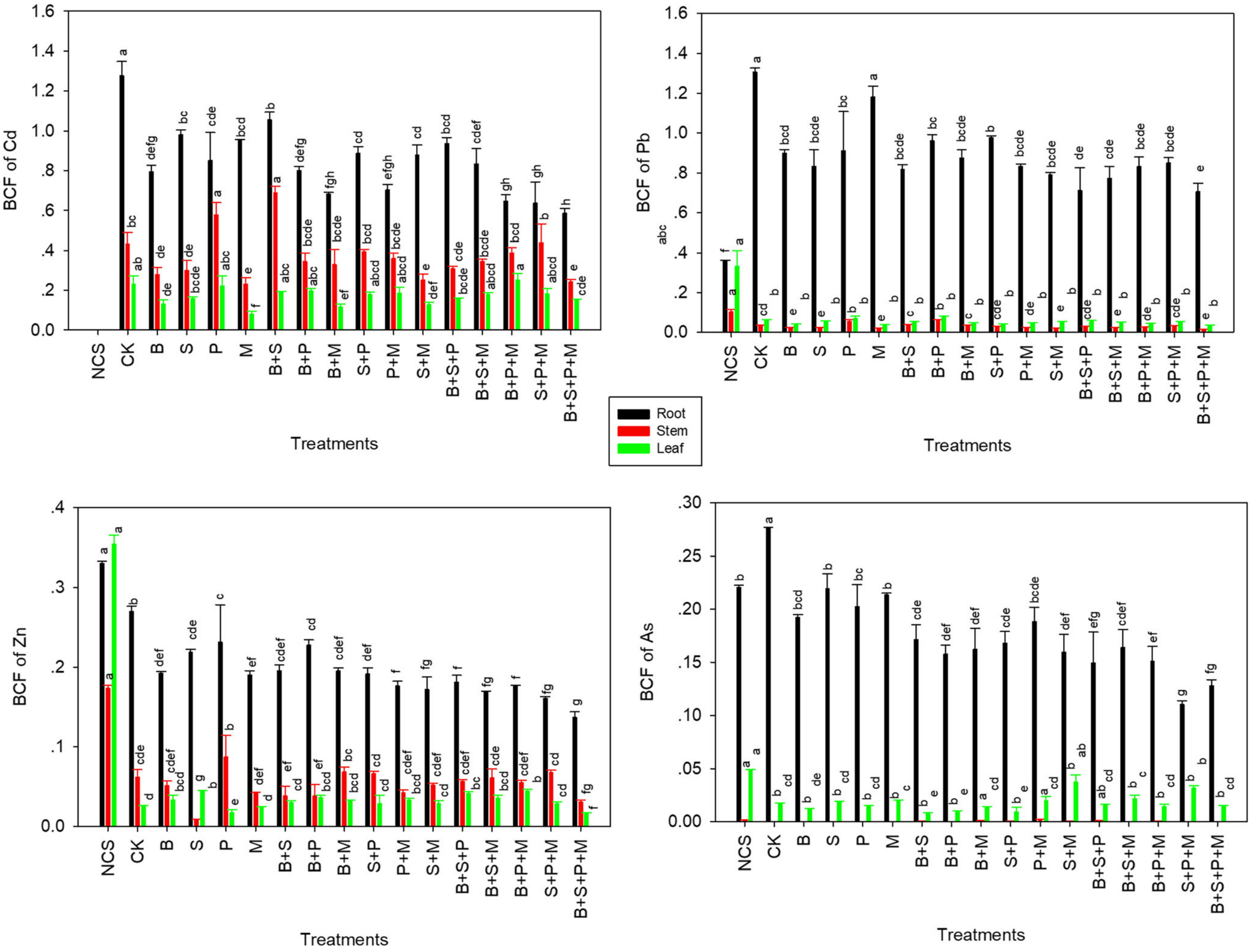

Fig. 6 BCF (bioaccumulation factor, the ratio of metal concentration in the plant root, stem, or leaf to the soil) of king grass in the pot test. Each data point represents the mean of triplicate determinations ± S.E. Different letters indicate significant differences between the means (LSD test, $p \leq 0.05$)

king grass cannot be directly used as green energy raw material after harvested from tailings. In order to reduce the environmental risk during the bioenergy recovery from king grass in heavy metal–contaminated tailings, the pretreatment techniques and thermochemical processes should be thoroughly explored in future research (Liu et al. 2012; Dastyar et al. 2019; Grottola et al. 2019).

The leaching of heavy metals in tailings is an important indicator of metal immobilization efficiency (Lee et al. 2014). However, in the present study, the pH and the content of Cd, Pb, Zn, and As of leachate in the CK treatment were similar to CK0 (Fig. 8 and Table 3), which indicated that the plants had little effect on the leaching of pH and heavy metals after phytostabilization (harvesting of plants). This may have been because planting plants on tailings may lead to the removal of heavy metals by plants, but the secretion of H^+ ions by plant roots and rhizosphere microorganisms in the tailings can increase the bioavailability of the metals (Alford et al. 2010; Vamerali et al. 2010; Sheoran et al. 2011; Ali et al. 2013). The negative and positive effects of these two aspects would cancel each. The changes in pH and metal concentrations with time under the different treatments in the leachate are shown in Fig. 8 and Table 3. The pH of exudate declined slowly and maintained at 6.0~6.6 after a leaching period of 30 days, which indicated that the tailings had an acid buffering capacity.

Generally, according to the surface water quality standard of China (GB3838-2002), the surface water quality is divided into five class based on their environmental functions and protection objectives. The water of V class is primarily suitable for agricultural use areas and general landscape requirements, and the threshold value required for the V class of the surface water quality standard of China is often chosen to assess water pollution. During the 30-day leaching period, the content of Cd, Pb, and Zn in the leachate in all of the treatments was 0.067~0.264, 0.206~0.509, and 3.215~14.46 mg L^{-1}, respectively, which was higher than the threshold values required for V class surface water quality

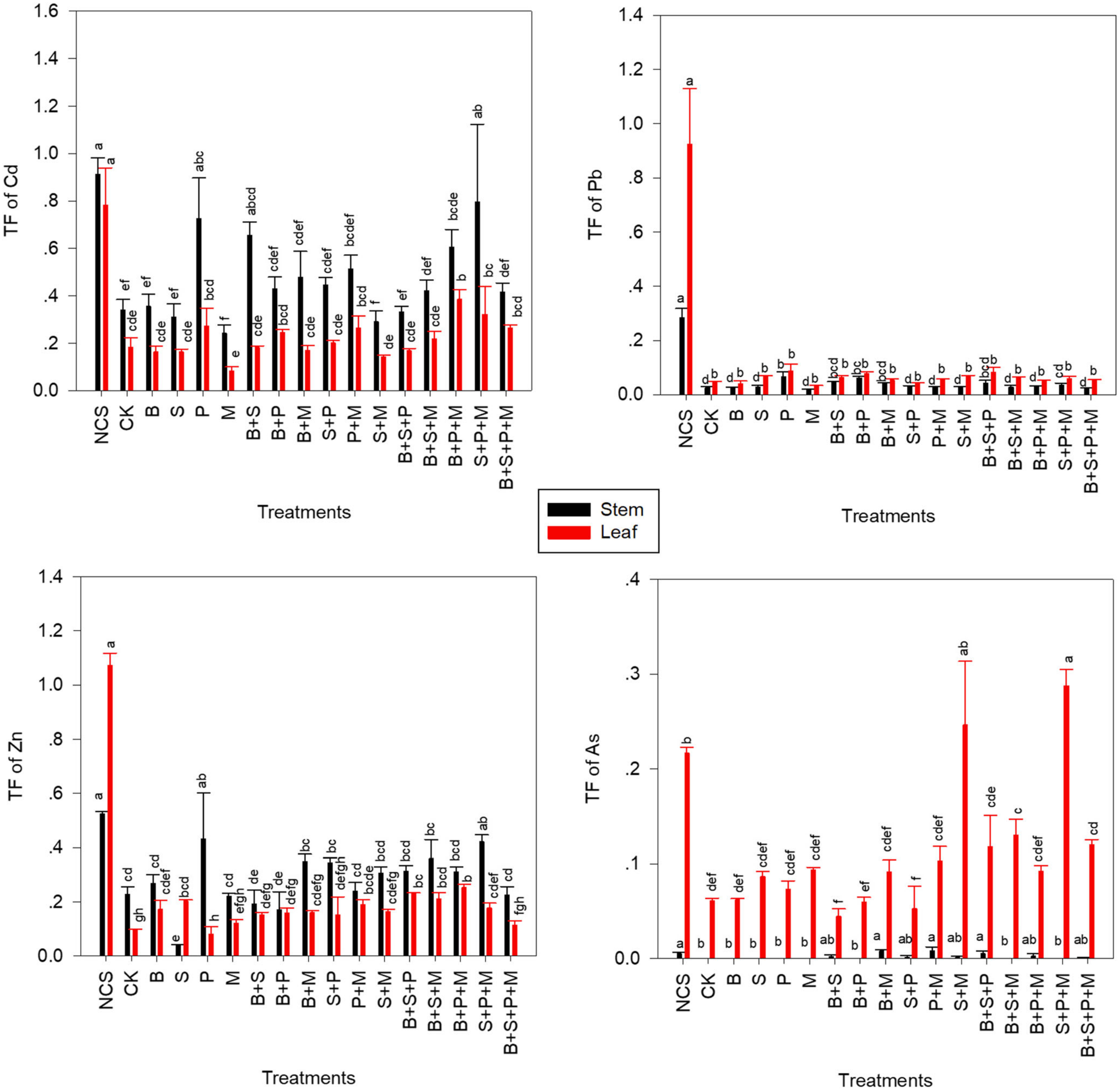

Fig. 7 TF (translocation factor, the ratio of metal concentration in the plant stem or leaf to the root) of king grass in the pot test. Each data point represents the mean of triplicate determinations ± S.E. Different letters indicate significant differences between the means (LSD test, $p \leq 0.05$)

standard of China (GB3838-2002, 0.01 mg L^{-1} for Cd, 0.1 mg L^{-1} for Pb, and 2 mg L^{-1} for Zn, respectively). However, the As content in all of the treatments was 20.66~45.27 μg L^{-1}, which was lower than the threshold values required for the V class surface water quality standard of China (GB3838-2002, 100 μg L^{-1}). These results indicated that lead-zinc ore tailings released large amounts of Pb, Zn, and Cd to the surrounding environment due to leaching. Furthermore, the content of Zn of the leachate in the B+S+P+M treatment was below the threshold value, while the content of Cd and Pb of the leachate was still higher than each threshold value even if the same treatment was performed. The results manifested that the B+S+P+M treatment was more effective in water purification of Zn than Cd and Pb. The tailing metal release process is divided into a rapid release process and a slow release process. The four kinds of heavy metal content (Cd, Pb, Zn, and As) of the exudate decreased rapidly with leaching time. The concentration of As tended to be stable and entered a slow release process on the 18th day, Pb on the 21st day, and Zn and Cd on the 24th day. This may

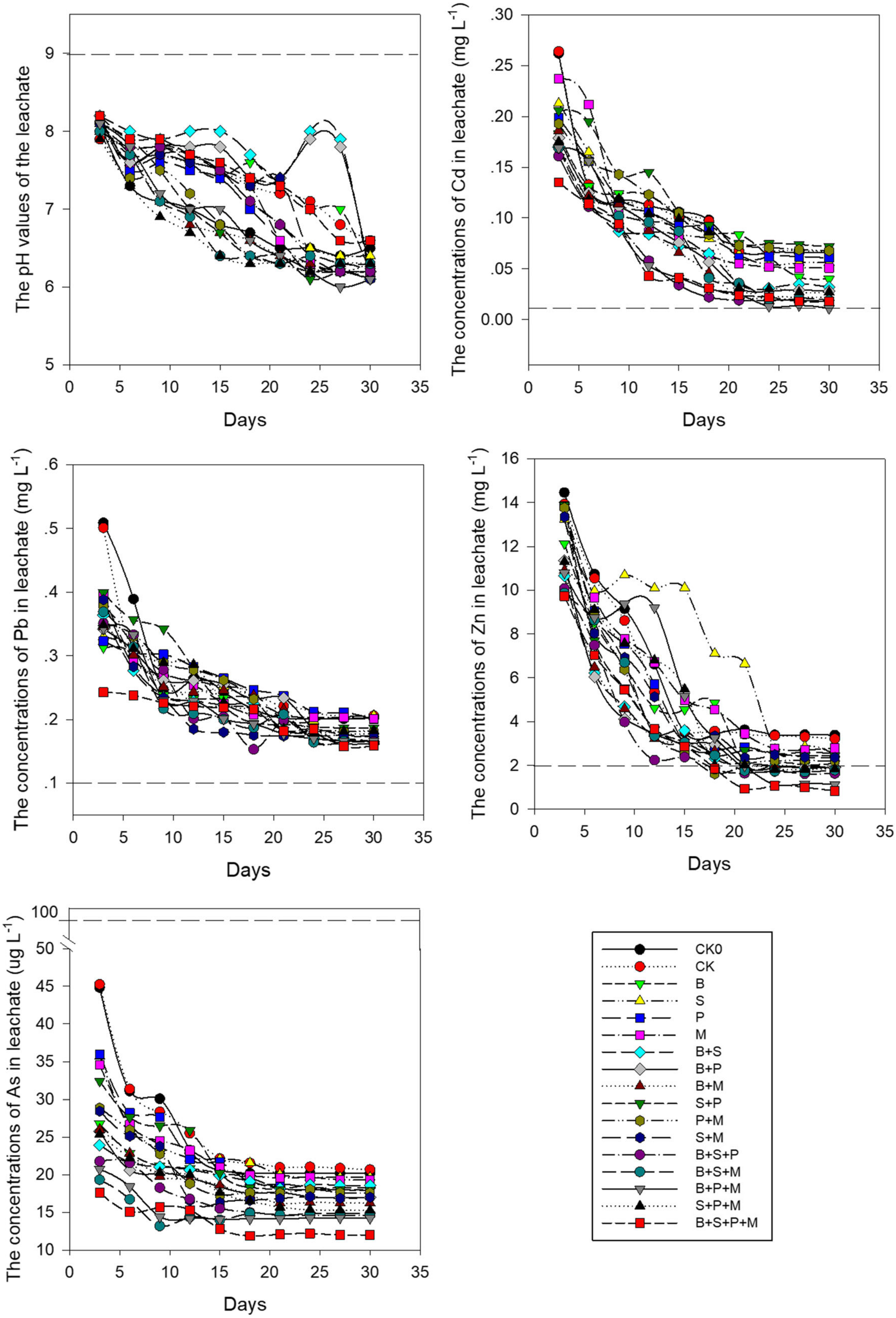

Fig. 8 The pH and metal concentrations in the leachate from the test columns. The dotted line represents the threshold values required for the V class surface water quality standard of China (GB3838-2002) (this water is primarily suitable for agricultural use areas and general landscape requirements)

Table 3 Average value of the pH and metal concentrations in the leachate from the test columns

Treatments	pH	Cd (mg L^{-1})	Pb (mg L^{-1})	Zn (mg L^{-1})	As (μg L^{-1})
CK0	6.89	0.109	0.267	6.166	25.06
CK	7.35	0.109	0.256	5.886	25.76
B	7.38	0.097	0.226	4.944	20.34
S	7.19	0.100	0.248	7.590	23.01
P	7.05	0.100	0.258	5.230	22.78
M	7.13	0.099	0.246	5.918	22.74
B+S	7.72	0.073	0.226	3.863	20.01
B+P	7.59	0.076	0.240	3.845	19.05
B+M	6.81	0.071	0.237	3.864	18.89
S+P	6.84	0.118	0.255	4.632	22.27
P+M	6.82	0.109	0.250	4.506	20.20
S+M	7.20	0.117	0.214	4.943	19.44
B+S+P	7.15	0.055	0.221	3.456	16.72
B+S+M	6.78	0.070	0.220	4.098	15.14
B+P+M	6.84	0.060	0.221	5.192	15.26
S+P+M	6.66	0.082	0.240	4.973	18.33
B+S+P+M	7.42	0.054	0.205	3.439	13.64
	6~9	0.01	0.1	2	100

The threshold values required for the V class of the surface water quality standard of China (GB3838-2002) (this water is primarily suitable for agricultural use areas and general landscape requirements)

have been because at the beginning of the leaching period, heavy metal ions adsorbed on the surface of the particle tailings would quickly dissolve into the leachate, and the hydrogen ions in acid rain would replace the exchangeable state of the heavy metal ions, resulting in heavy metal ions being rapidly released. As time goes on, iron manganese bound and the organic bound state of heavy metal in the tailings would release slowly (Barajas-Aceves et al. 2015). Therefore, more attention should be paid to the environmental pollution caused by the leaching of heavy metals in tailings during the prophase after phytostabilization (harvesting of plants).

The addition of amendments could significantly reduce the content of Cd, Pb, Zn, and As of the leachate in tailings. During a 30-day leaching period, the average decrease in the content of Cd, Pb, Zn, and As was −7.52~50.46%, −0.90~20.04%, −28.96~41.58%, and 1.35~47.04%, respectively, for the different amendment treatments. The passivation effect of heavy metal in the B+S+P+M treatment, which had four amendments added (0.1% biochar+2.5% NCS+0.5% peat+0.25% manure), had the best outcome of all of the treatments. This may have been because amendments, such as biochar, non-contaminated soil, peat, and manure, chelated and adsorbed with the heavy metal, and this reduced the activity and exchangeable state of heavy metals in the tailings (Rodríguez et al. 2016). The metal contents of the leachates in the treatments with biochar were lower than those in the treatments without biochar. In the treatment of two kinds of amendments, the metal contents of the leachates in the treatments with B+S, B+P, and B+M were lower than those in the other three treatments of S+P, P+M, and S+M. In the treatment of three kinds of amendments, the metal contents of the leachates in the treatments with B+S+P, B+S+M, and B+P+M were lower than those in the treatments with S+P+M. These results indicated that the biochar had a higher immobilization capacity for Cd, Pb, Zn, and As than organic manure, peat, and non-contaminated soil. These results are similar to those of previous studies, which reported that biochar application reduced the Cd (57~73%), Pb (45~55%), and Zn (46%) concentrations in the leachate of the mining soil (Puga et al. 2016).

Conclusion

This pot test verified that lead-zinc ore tailings release large amounts of Cd, Pb, and Zn into the surrounding environment by leaching. However, the combined effect of amendments and plants could significantly reduce this risk. Biochar had a higher immobilization capacity for Cd, Pb, Zn, and As than manure, peat, and non-contaminated soil. The combination of all four amendments (biochar, manure, peat, and non-contaminated soil) showed the least amount of metal uptake into the king grass and the most reduction in metal leaching. Generally, the BCF of Cd and Pb in the plant roots were high, while the BCF of Zn and As in the plant roots were relatively low. Therefore, the combination of all four amendments could be appropriate for pollution reduction, and king grass is a suitable plant for phytostabilization of Cd and Pb in lead-zinc mine tailings. After phytostabilization (harvesting of the plants), the plants had little effect on the leaching of Cd, Pb, Zn, and As, while the amendments significantly reduced the contents of Cd, Pb, Zn, and As in the leachate of tailings. However, it is necessary to conduct field tests in future research to confirm whether the same effect found in the pot test can be actually obtained in the field. In addition, studies need to be performed to find out if the application rate is realistic in terms of cost.

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