RESEARCH ARTICLE



Influence of CaO-activated silicon-based slag amendment on the growth and heavy metal uptake of vetiver grass (*Vetiveria* zizanioides) grown in multi-metal-contaminated soils

Jing Mu^{1,2,3} • Zhengyi Hu^{1,3,4} • Zijian Xie¹ • Lijuan Huang^{1,2,3} • Peter E. Holm^{2,3}

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Abstract

Few plant species used for revegetation grow well in multi-metal-contaminated soils. Vetiver grass (*Vetiveria zizanioides*) is known to be tolerant of heavy metals. Vetiver has been reported to be effective for revegetation and heavy metal phytoextraction by applying targeted amendments due to its large biomass. In this study, a greenhouse vetiver pot experiment and soil incubation were performed to investigate the growth and Cd, Cr, Cu, Pb, and Zn uptake of vetiver grown in multi-metal-contaminated soils treated with a CaO-activated Si-based slag amendment (0, 0.5, 1.0, and 2.0% w/w). The results showed that the effects of slag amendment on plant growth and heavy metal uptake and distribution were dependent on the amendment dosages and metal species. Although vetiver could grow in contaminated soils, its growth was obviously inhibited. The slag amendment enhanced the vetiver growth and the highest biomass (2.62-fold over the control) was determined at a 1.0% amendment rate. The slag amendment improved plant growth by alleviating the toxicity of heavy metals in plants. This result was mainly attributed to the increases in soil pH and citric acid-extractable Si caused by alkaline amendment. The results suggest that vetiver can be applied to remediate multi-metal-contaminated soils in conjunction with the application of CaO-activated Si-based slag amendment.

 $\textbf{Keywords} \ \ Vetiver \ grass \cdot Si\text{-based slag amendment} \cdot Multi\text{-metal-contaminated soils} \cdot Revegetation \cdot Phytoextraction \cdot Phytostabilization$

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- Zhengyi Hu zhyhu@ucas.ac.cn
- Peter E. Holm peho@plen.ku.dk
- College of Resources and Environment, University of Chinese Academy of Sciences, Beijing 101408, China
- Department of Plant and Environmental Sciences, University of Copenhagen, Thorvaldsensvej 40, 1871 Frederiksberg, Denmark
- Sino-Danish Center for Education and Research (SDC), Beijing, China
- ⁴ Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Introduction

According to the Ministry of Environmental Protection and Ministry of Land and Resources (China 2014), the overall percentage of national soil exceeding the environmental quality standard for soil in China is 16.1%. Inorganic pollutants, including cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), zinc (Zn), arsenic (As), mercury (Hg), and nickel (Ni), account for 82.8% of the total contamination. The heavy metalcontaminated sites are primarily caused by five key industries, including lead battery manufacturing, electronic component manufacturing, metal surface and heat treatment processing, non-ferrous metal smelting, and raw chemical material manufacturing (Song et al. 2014). Metal pollution can be distributed across large distances as a result of wind transfer, surface erosion, and leaching (Radziemska et al. 2017). Therefore, the restoration of heavy metal-contaminated soil has become a major and urgent task for environmental protection in China.

The ideal method for restoring heavy metal-contaminated soils is to remove the heavy metals from the soil to concentrations that are close to or meet the background value or

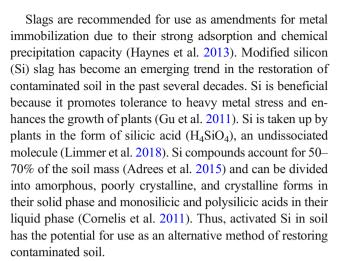


standard of soil metals. The restoration of multi-metal-contaminated soils is difficult because the diverse properties of metals and metalloids, such as Cd, Cu, Cr, Pb, and Zn, can be immobilized in the soil by sorption, precipitation, and complexation reactions; however, these elements can also be removed from soil by plant uptake, leaching, and volatilization (Bolan et al. 2014). Soil washing technology has a high cost and poses a potential risk of groundwater pollution (Dermont et al. 2008). Revegetation can assist in stabilizing and minimizing the wind dispersion and migration of heavy metals through soil via water (Radziemska et al. 2017). However, limitations of revegetation include low soil fertility and heavy metal toxicity in contaminated soils (Zhang et al. 2016). Thus, selecting the appropriate plant species is the main factor dictating the success of revegetation.

Hyperaccumulator plants absorb high levels of specific metals in their aboveground structures. Several plant cultivars are known for their effectiveness in revegetation, such as the grass *Vetiveria zizanioides*, the herbaceous legume *Sesbania rostrate*, and the woody legume *Leucaena leucocephala* (Wong 2003). However, such plants are usually ineffective for large-scale phytoremediation of multi-metal-contaminated soils due to their slow growth and low productivity (Mahar et al. 2016), which result from non-specific heavy metal toxicity in hyperaccumulators.

Vetiver grass (Vetiveria zizanioides) is a promising plant for revegetation and the phytoextraction of multiple heavy metals in contaminated soils. This species is perennial and tall (at a maximum of 2 m) and displays rapid growth, high biomass production, and a long root system (up to 4.6 m) (Chen et al. 2004). Furthermore, vetiver is highly tolerant to elevated levels of heavy metals, such as Cd, Cu, Pb, and Zn (Banerjee et al. 2016). Vetiver has been applied for the phytostabilization of metal pollution (Ghosh et al. 2015) and to prevent contaminants from leaching into the groundwater and running off into surface water bodies. The accumulation of Cd in the aboveground portions of vetiver was reported to be even greater than that of a hyperaccumulator because of the former's high biomass (Chen et al. 2000). However, the effects of vetiver on multi-metal-contaminated soils remain poorly investigated.

Plant growth is affected by the solubility of toxic metals and nutrients in contaminated soils. Thus, soil amendments are necessary for the establishment of vegetation in contaminated soils (Yang et al. 2003). In particular, amendments for improving the revegetation and productivity of plants can reduce the solubility, leaching, and bioavailability of heavy metals by regulating soil pH and increasing nutrient availability (Mahar et al. 2016; Wen et al. 2016). The most widely applied amendments include organic matter, lime, nanohydroxyapatite, fertilizers, and mineral materials (Lahori et al. 2017).



In the present study, a combination of vetiver and CaO-activated Si-based slag amendment was implemented to remediate multi-metal-contaminated soils. The objectives of this study are to evaluate (1) the effects of amendment on the immobilization of heavy metals in multi-metal-contaminated soils, (2) the potential growth and heavy metal uptake of vetiver grown in multi-metal-contaminated soils, and (3) the effects of CaO-activated Si-based slag amendment on the vetiver plant growth and heavy metal uptake by vetiver. This study could provide a practical basis for field-scale remediation of multi-metal-contaminated soils, thus achieving rapid revegetation and sustainable remediation of multi-metal-contaminated soils.

Materials and methods

Soil

The contaminated soil samples were collected from the vicinity of a former battery factory (approximately 6 ha) in Fuyang City, Anhui Province, China, in May 2017. The battery factory was established in 1973 and originated from a lead smelting industry with approximately 150 years of history. This site was polluted mainly by industry, and little by agriculture. The sampling area presents a north subtropical humid monsoon climate, an annual average temperature of 14.4 °C, average sunshine of 2070 h, an average rainfall of 1421 mm, and an average evaporation of 1389 mm. In addition, northerly winds occur in winter, and southerly winds occur in summer.

The top soil layer (0–20 cm) was sampled for the present soil incubation and greenhouse vetiver pot experiments. The soil was thoroughly mixed, air dried, and passed through a 2-mm sieve. The soil properties are shown in Table 1.

The soil samples were analyzed according to the recommended analytical methods for soil and agricultural chemistry (Lu 1999). Soil pH (soil:water, 1:2.5) was measured using an HI98185A type pH meter (Hanna, Italy). The soil organic



 Fable 1
 Properties of soil and amendment used in this study

Materials	Hd	Citric acid-extractable Si (mg kg ⁻¹)	${\rm Cr} \\ {\rm (mg~kg}^{-1}$	Pb	Cu	Zn	Cd	$\begin{array}{cc} \text{Cd} & \text{OM} \\ \text{(g kg}^{-1}) \end{array}$	CEC (cmol kg ⁻¹)	${\rm TN} \\ ({\rm g~kg}^{-1})$	Olsen-P (mg kg ⁻¹)	Available K (mg kg ⁻¹)	Clay (%)	Silt	Sand
Soil	7.9	868.2	148.3	76.1	28.5	91.2	2.6 18.5	18.5	25.0	1.2	21.2	120.0	18.1	41.5	40.4
Amendment	12.3	611.0	59.7	30.1	564.8	228.0	I	I	I	1	I	I	ı	ı	ı

OM, organic matter; CEC, cation exchange capacity; TN, total nitrogen; Olsen P, bicarbonate extractable

matter was determined by the potassium dichromate oxidation-ferrous sulphate titrimetry method (Nelson and Sommers 1996). The CEC was determined using the 1.0 M CH₃COONH₄ leaching method at a pH of 7.0. The soil particle-size distribution was determined with the pipette method. The total N was determined by micro-Kjeldahl digestion followed by steam distillation. The available P was extracted using 0.5 M NaHCO₃ and determined by the molybdenum blue method. The available K was extracted using 1.0 M CH₃COONH₄ and determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, Perkin Elmer, Optima 5300DV, USA). The available Si was extracted using 0.25 M citric acid and analyzed by Si molybdenum blue spectrophotometry. The available concentrations of Cd, Cr, Cu, Pb, and Zn in soils were determined by the AB-DTPA method and analyzed by the ICP-OES. The total Cd, Cr, Cu, Pb, and Zn contents of soil were measured by the ICP-OES after microwave digestion with HNO3-HF according to the USEPA method 3052 (USEPA 1996). Standard soil reference materials (GBW-07405, China National Centre for Standard Materials) were used for quality control of the analytical procedure. The recovery rates for heavy metals were within $90 \pm$ 10%. The soil Cd exceeded the risk screening value for the Risk Control Standard for Soil Contamination of Agricultural Land in China (GB15618-2018).

Si-based slag amendment

The CaO-activated Si-based slag amendment was derived from Cu tailings after acid leaching, which were obtained from the Cu tailing pond of Sanfengshan Gold Mine Limited Liability Company, Ruoqiang County, Xinjiang Uygur Autonomous Region, China. The slag amendment was ground to a fine powder and sieved at < 0.178 mm. The amendment properties are shown in Table 1.

The slag amendment was digested using a microwave digester (Mars6, CEM Corporation, USA) with HNO3-HF according to the method 3052 (USEPA 1996). Blanks and certified references of Cu mine samples (GBW (E) 070074, National Institute of Metrology, China) were included to ensure the reproducibility and accuracy of the measurements. The recovery of metals was in the range of 95–110%. The concentrations of heavy metals after digestion were analyzed by the ICP-OES (USEPA 1996). The pH (sample:water at 1:5) was measured using a pH meter. Available Si was extracted using 0.25 M citric acid and analyzed by the Si molybdenum blue spectrophotometry (Lu 1999). The chemical composition of the slag amendment was determined by an X-ray fluorescence spectrometer (XRF-1800, Shimadzu, Japan) (Hu et al. 2017). The surface area and pore distributions of the slag amendment were measured with a Quadrasorb SI-MP surface area analyser (Quantachrome, USA). The contents of heavy metals were lower than the standards for fertilizers in China



(GB/T 23349-2009). The slag amendment contained 25.83% CaO, 19.81% Fe₂O₃, 13.91% S, 13.62% Na₂O, 1.01% Al₂O₃, and 0.19% MgO. The specific surface area of the slag amendment was $1.08~{\rm m}^2~{\rm g}^{-1}$, the total pore volume was $0.008~{\rm cc~g}^{-1}$, and the average pore size was 309 nm.

Pot experiment and soil incubation

The effect of Si-based slag amendment on the remediation of multi-metal-contaminated soil was evaluated by greenhouse vetiver pot experiments (with plants) and soil incubation (without plants). For the greenhouse vetiver pot experiment, four treatments were applied: a control treatment with no amendment (CK) and three levels of slag amendment (0.5%, 1.0%, and 2.0% (w/w)). Three replicates were employed for each treatment, with a total of 12 pots. 1.5 kg of soil was packed into each pot (14 cm diameter and 16.5 cm height). The slag amendments were thoroughly mixed with soil. The soil in each pot was supplied with 0.2 g N kg $^{-1}$ soil as NH₄NO₃, 0.15 g P kg $^{-1}$ soil as Ca(H₂PO₄)₂, and 0.15 g K kg $^{-1}$ soil as K₂SO₄ as the base fertilizers. The fertilizers were added to the soil in solution. Nutrient solutions were mixed thoroughly with the soil/amendment mixture prior to potting.

The pot soil was kept moist (12%, w/w) for 1 week of equilibrium in a greenhouse. Three tiller seedlings of 3month-old vetiver (shoot and root lengths in 20 cm and 5 cm, respectively) were transplanted into each pot soil. The water content was kept at 70% of the soil's water holding capacity via the addition of deionized water for the entire growth period by weight measurement. Plants were grown in the greenhouse under natural sunlight conditions (temperature 20-30 °C, daytime 13-14 h, and relative humidity 30-50%) for 63 days. All pots were arranged randomly in the greenhouse. Soil pore water samples were extracted at the 21st day and 63rd day of planting from each pot using Rhizon soil moisture samples (SMS, model MOM, Rhizosphere Research Products, Netherlands) with a nominal porosity of 0.15 µm. Immediately after collection, measurements of the soil pore water samples were conducted to determine the pH, total organic carbon (TOC), Si and heavy metal concentrations. The TOC was measured using a TOC analyser (Multi N/C 3100, Analytik Jena, Germany). The Si concentration was determined by the ICP-OES. The heavy metal concentrations were determined by ICP-MS.

Vetiver plants were harvested at 63 days after planting. The vetiver from each treatment was divided into two parts (shoots and roots) and rinsed with deionized water. Then, the shoot and root lengths were recorded. The tissues were heated at 105 °C for 30 min (Yan et al. 2017), oven dried (48 h at 70 °C), and weighed until they reached a constant weight, and then, the dry weight (DW) of the shoots and roots was recorded. The dried plant samples were ground and sieved with a 0.5-mm sieve for analysis. The soil sample in each

pot was air-dried at room temperature, ground until thoroughly homogenized, and sieved with 2-mm and 0.15-mm sieves for analysis. Plant samples were digested with HNO₃-H₂O₂ in a microwave digester (see above) according to the method 3050B (USEPA 1996). Zn concentrations were determined by the ICP-OES. The concentrations of Cd, Cr, Pb, and Cu in the digestion were determined by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer, ELAN DRCe, USA). The Si concentration of plants was determined by the ICP-OES after microwave digestion with a mixture of HNO₃, HCl, and HF (Novozamsky et al. 2008). Blank and standard reference materials of plants (GBW-07605, tea leaves, China National Centre for Standard Materials) were used for quality control of the analytical procedures. The recovery rates for heavy metals were within $90 \pm 10\%$. Soil samples were submitted to measure soil pH; citric acid-extractable Si; DTPAextractable Cd, Cr, Cu, Pb, Zn; and total Cd, Cr, Cu, Pb, and Zn concentrations. The analytical methods of these soil properties were the same as those described above.

For the soil incubation experiment, the slag amendment was thoroughly mixed with 1.5 kg of soil at the rates of 0.5%, 1.0%, and 2.0% (w/w). Soil without the slag amendment was designated as the control. Three replicates were employed for each treatment. The soil was also supplied with $0.2 \text{ g N kg}^{-1} \text{ soil as NH}_4\text{NO}_3, 0.15 \text{ g P kg}^{-1} \text{ soil as}$ Ca(H₂PO₄)₂, and 0.15 g K kg⁻¹ soil as K₂SO₄ as fertilizers. The fertilizers were added to the soil in solution and mixed thoroughly, and the samples were then placed in plastic containers (14 cm diameter and 16.5 cm height). All containers were capped with a plastic cover that had a small hole for gas exchange and to minimize moisture loss. The containers were arranged in a randomized block design and incubated for 63 days. The other procedures and soil sampling were the same as those described in the greenhouse vetiver pot experiment.

Data analysis and statistics

The translocation factor (TF) is defined as the ratio of the metal concentration in the shoots to that in the roots. The TF value is used to measure the efficacy with which a plant translocates heavy metals (Christou et al. 2017). The bioaccumulation factor (BCF) is defined as the ratio of heavy metal concentration in the shoot or root of a plant to that in the soil (Mohamed et al. 2015). The BCF value is used to estimate the potential of a plant for phytoremediation (Galal and Shehata 2015).

All data were expressed as the mean of three replications. Statistical analyses (one or two-way ANOVA) were performed using SPSS version 19.0 software (SPSS Inc., Chicago, USA). Least significant difference (LSD) was used to test for significance at p < 0.05 between the means. Pearson correlations were also performed using the SPSS, and values were considered significant at p < 0.05 and p < 0.01.



Results and discussion

Effect of the slag amendment on the properties of soil pore water

The effect of slag amendment on the pH of soil pore water differed with the planting time (Table 2). Compared with CK, the application of amendment in the contaminated soils increased the pH of soil pore water by 0.14-0.73 on the 21st day of planting but decreased the pH of soil pore water by 0.1-0.21 on the 63rd day of planting (Table 2). The effect on the 21st day sampling could be explained by the presence of the alkaline amendment (pH 12.25) resulting in an increase in the pH of the soil pore water pH. This is in line with Houben et al. (2012) who observed that the application of CaCO₃ in metalcontaminated soils raised the pH (from 8.0 to 8.4) in the leachates collected in the second week of planting. The decreased pH in pore water on the 63rd day could be attributed to the plant release of protons into the rhizosphere, as the roots had grown large at day 63. Ashrafi et al. (2015) also observed that the pH in the leachates of soils with banana-stem alkaline amendments (pH 8.89) was lower than that without the amendment (7.4 vs. 7.7).

No significant differences in the TOC of the pore water of CK soils were observed on the 21st day and 63rd day of planting. The TOC in soil pore water of the amended soils on the 21st day of planting was 2.45–6.75 times the value on the 63rd day of planting (Table 2), because the amendment effectively accelerated the decomposition of organic matter at

the early stage of vetiver growth. On the 21st day, TOC in soil pore water was significantly increased with the increasing application of amendment (Table 2). On the 63rd day, the amendment significantly increased TOC in soil pore water only with 2.0% amendment, but not with 0.5% and 1.0% amendments, in comparison with CK (Table 2). These results could be ascribed to the decomposition of organic matter in soils at different pH levels (7.79 vs 7.93–8.52) (Zheng et al. 2012). The decomposition resistance of organometallic complexes could also explain the higher TOC in soil pore water with a higher application rate of amendment (Table 2).

The Cd, Cr, and Pb were not detected in the pore water of contaminated soils on the 21st and 63rd days of planting with or without the amendment. This result could be explained by the increase in the retention of cationic heavy metals on the soil surface because the number of negatively charged sites on the soil surface increases with increased pH (Zheng et al. 2012). Similarly, Lim et al. (2013) observed that applying a lime-based amendment significantly immobilized Cd and Pb through increased soil pH.

The Zn was detected in the pore water of the contaminated soils with and without amendments on the 21st day and 63rd day of planting (Table 2), which could be related to the high concentration of Zn in the tested soils. Additionally, Cu was detected in the pore water with a high rate of the amendment on the 21st day and 63rd day (Table 2), which could be attributed to the Cu-containing amendment itself (564.8 mg kg⁻¹). Generally, concentrations of Zn in the soil pore water on the 63rd day were higher than those on the 21st day with or without the amendment, which could be attributed to the

Table 2 Effect of the CaO-activated Si-based slag amendment on the pH and concentrations (mg L^{-1}) of TOC, Si, Cu, and Zn in the pore water of contaminated soils planted with vetiver

Incubation time (day)	Application rate (%)	рН	TOC	Si	Cu	Zn
21	CK	$7.79 \pm 0.18 \text{ b}$	$16.13 \pm 0.15 \text{ d}$	14.03 ± 0.13 d	< LOD	$0.06 \pm 0.00 \text{ a}$
	0.5	$7.93 \pm 0.02 \ b$	36.90 ± 2.13 c	$23.31 \pm 0.19 \ b$	< LOD	0.06 ± 0.01 a
	1.0	$8.02 \pm 0.12 \ b$	$70.27 \pm 3.31 \ b$	28.06 ± 2.17 a	$0.02 \pm 0.01 \ b$	$0.04 \pm 0.01 \ b$
	2.0	8.52 ± 0.09 a	209.4 ± 8.09 a	$18.36 \pm 1.82 \ c$	$0.08\pm0.00~a$	$0.03 \pm 0.01 \ b$
63	CK	7.70 ± 0.15 a	$15.85 \pm 1.67 \ b$	14.25 ± 0.46 c	< LOD	$0.11 \pm 0.01 \ b$
	0.5	$7.49 \pm 0.04 b$	$15.09 \pm 3.31 \text{ b}$	$18.69 \pm 1.89 \ b$	< LOD	$0.28\pm0.02~a$
	1.0	$7.60 \pm 0.07 \ ab$	$15.90 \pm 2.17 b$	$19.10 \pm 0.51 \ b$	< LOD	$0.09\pm0.00\;b$
	2.0	$7.59 \pm 0.03 \text{ ab}$	$31.03 \pm 5.10 \text{ a}$	24.76 ± 0.65 a	$0.01\pm0.00~a$	$0.10 \pm 0.04 \ b$
Analysis of variance for	incubation time (21 vs. 63)					
CK		ns	ns	ns	_	<i>p</i> < 0.01
0.5		p < 0.01	p < 0.01	p < 0.05	_	p < 0.01
1.0		p < 0.01	<i>p</i> < 0.01	p < 0.01	p < 0.05	p < 0.01
2.0		p < 0.01	<i>p</i> < 0.01	<i>p</i> < 0.01	p < 0.01	p < 0.05
Application rate × incuba	ation time	p < 0.01	p < 0.01	p < 0.01	p < 0.01	p < 0.01

LOD, limit of detection; ns, non-significant. CK = control: 0.5 = 0.5% amendment; 1.0 = 1.0% amendment; 2.0 = 2.0% amendment. Means followed by different letters in each column within an incubation time are significantly different (p < 0.05)



differences in pH in the soil pore water during the two planting time periods (Table 2). The increase in pH induced a reduction in the number of positively charged sites in the soil.

The Si concentration in pore water was higher in the amended soils than in CK treatment (Table 2), which could be attributed to the pH-induced dissolution of soil Si with the application of amendment (Table 3) along with the Si contained in the amendment (611 mg kg⁻¹) (Zheng et al. 2012). No significant differences in the Si content of the pore water in CK treatment were observed between the 21st day and 63rd day of planting (Table 2). However, the Si concentrations in the pore water collected on the 63rd day were lower than those on the 21st day with the 0.5% and 1.0% amendment treatments. Moreover, at a high rate of amendment, the concentrations of Si in the pore water collected on the 63rd day were higher than those on the 21st day (Table 2), which could be related to differences in the uptake of Si in vetiver among the treatments during the two growth stages. The formation of silicate precipitates in soil decreased the Si concentration during the early stages of organ development (Zheng et al. 2012). The coprecipitation of Si-metal complexes seems to contribute to cell detoxification, thereby promoting the growth of plants and ultimately leading to increased Si accumulation in the plants themselves (Adrees et al. 2015).

Effect of the slag amendment on the available Si and heavy metals in soils

The slag amendment significantly affected the citric acid-extractable Si in soils (Table 3). In unplanted soils, the application of amendment increased the citric acid-extractable Si in soils by 14.6–45.4% compared with that in CK because the amendment has abundant citric-extractable Si (611 mg kg⁻¹). The concentration of citric acid-extractable Si in soils planted with vetiver was lower with the amendment than in CK

Table 3 Effect of the CaO-activated Si-based slag amendment on concentrations (mg ${\rm kg}^{-1}$) of citric acid-extractable Si in contaminated soils during incubation for 63 days (unplanted) and after harvesting vetiver on the 63rd day (planted)

Application rate (%)	Unplanted	Planted
CK	511.19 ± 3.62 d	741.89 ± 27.49 a
0.5	$632.36 \pm 18.01 \text{ b}$	505.34 ± 6.34 c
1.0	585.86 ± 36.08 c	$451.32 \pm 30.82 d$
2.0	743.49 ± 18.72 a	$654.78 \pm 32.28 \text{ b}$
Analysis of variance		
Planted Application rate Planted × application rate	p < p < p <	0.01

CK = control: 0.5 = 0.5% amendment; 1.0 = 1.0% amendment; 2.0 = 2.0% amendment. Means followed by different letters within columns are significantly different (p < 0.05)



(Table 3), and this effect could be ascribed to the differences in the growth and concentration of Si in vetiver (Table 6).

Application of amendment significantly decreased DTPAextractable Cd, Cr, and Pb in soils (Table 4). Three principal mechanisms could explain these results. First, the application of amendment increased the precipitation of Cd, Cr, and Pb due to the amendment-induced increase in soil pH (Table 2). Application of the alkaline amendment was reported to increase the soil pH, thereby decreasing the DTPA-extractable Cd and Pb in soils planted with Chinese cabbage or maize (Chang et al. 2013; Lim et al. 2013). The low concentration of DTPA-extractable Cr indicated that the soil Cr mostly occurs in the form of Cr(III), which is stable in the soil. The increased soil pH may promote Cr(III) sorption by the soil organic matter (Hattab et al. 2014). Second, the amendment enhanced the stabilization of Cd, Cr, and Pb in soils, as the present amendment contained 19.8% Fe₂O₃, and Fe-rich amendments were reported to act as stabilizers of heavy metals (Lee et al. 2014). The third reason involved the coprecipitation of Cd, Cr, and Pb with silicic acid, which originated from the present amendment and from soil Si activated by the amendment-induced pH increase (Table 2). Gu et al. (2011) reported that Si-rich amendments significantly decreased the available Cd and Pb concentrations in soils.

The application of amendment increased the DTPA-extractable Cu in soils (Table 4), which could be explained by the present amendment containing Cu (564.8 mg kg⁻¹). The findings of the present study are consistent with Chiu et al. (2006) who found that the application of Cucontaining manure compost and sewage sludge in vetivergrowing soils increased the DTPA-extractable Cu. Frequent use of the amendment is not recommended because vetiver is a perennial plant. Heavy metals can be removed by harvesting vetiver shoots several times per year.

The application of amendment had no significant effect on DTPA-extractable Zn in soils (Table 4). In general, Zn is relatively insoluble at pH > 7; therefore, this result could be related to the high pH of the tested soil (7.9). Furthermore, the uptake of Zn in vetiver was the highest among the heavy metals (Table 7) since Zn is an essential nutrient for vetiver.

Effect of the slag amendment on the growth and biomass of vetiver

Vetiver can grow in multi-metal-contaminated soils without the application of amendment. Visual symptoms of phytotoxicity, such as abnormal colour or wilt, were not observed. This finding suggested that vetiver could tolerate multi-metal composite pollution.

Vetiver growth appeared to be strong in contaminated soils with the application of amendment. The root length of vetiver grown in contaminated soils was greater with the application of amendment than in CK. The greatest root length of vetiver

Table 4 Effect of the CaOactivated Si-based slag on the concentrations (mg kg⁻¹) of DTPA-extractable Cd, Cr, Cu, Pb, and Zn in contaminated soils after harvesting vetiver on the 63rd day

Application rate (%)	Cd	Cr	Cu	Pb	Zn
CK	0.64 ± 0.11 a	0.03 ± 0.01 a	$3.50 \pm 0.28 d$	42.69 ± 1.76 a	1.42 ± 0.13 a
0.5	$0.48\pm0.06\;b$	$0.02\pm0.00\ b$	4.04 ± 0.03 c	31.61 ± 1.63 bc	1.32 ± 0.12 a
1.0	$0.46\pm0.08\ b$	$0.02\pm0.00\ b$	$5.06 \pm 0.10 \ b$	$34.97 \pm 3.66 \ b$	1.54 ± 0.24 a
2.0	$0.43\pm0.05\ b$	$0.02\pm0.00\ b$	6.03 ± 0.23 a	$27.87 \pm 1.38\ c$	1.68 ± 0.24 a

CK = control: 0.5 = 0.5% amendment; 1.0 = 1.0% amendment; 2.0 = 2.0% amendment. Means followed by different letters within columns are significantly different (p < 0.05)

was observed with 0.5% amendment (Table 5). Excessive amendment inhibited the root length, which could be explained by heavy metal stress due to the increased concentrations of heavy metals in the roots under higher amendment rates (Table 7). However, the plant height of vetiver was lower with the application of amendment than in CK, and the shortest plant height for vetiver was obtained with 2.0% amendment (Table 5). Thus, vetiver grew short and strong on multi-metal-contaminated soils with the application of amendment, which was beneficial for the revegetation of multi-metal-contaminated soils.

The application of amendment resulted in a significant (p < 0.05) increase in the dry weight of shoots and roots by 127.6–190.3% and 14.8–164.2%, respectively (Table 5). The highest shoot dry weight of vetiver was obtained with 1.0% amendment, whereas the greatest root dry weight was obtained with 0.5% amendment (Table 5). The reduction in shoot and root dry weight under 2.0% amendment may be attributed to Cu toxicity since the amendment contained 564.8 mg kg⁻¹ Cu.

The highest biomass of vetiver was observed with 1.0% amendment (Table 5), which was 2.64 times the biomass of the vetiver with CK treatment. The amendment improved vetiver growth due to the alleviation of heavy metal toxicity in plants, although an excessive application of slag amendment (above 1.0%) tended to reduce the biomass of vetiver.

Effect of the slag amendment on concentrations of heavy metals and Si in vetiver

The concentrations of Si in the roots of vetiver were greater with amendment than with CK and increased as the

application rate of amendment increased (Table 6). This finding could be ascribed to the amendment-induced increase in the bioavailability of Si in soil pore water (Table 2). However, the concentrations of Si in the shoots of vetiver was lower with amendment than with CK (Table 6). The application of amendment increased the pH in the soil and pore water (Table 2), thereby resulting in an accumulation of Si-metal complexes in roots and restricting its transport to the shoots. This finding revealed that the application of amendment induced an accumulation of Si in the roots of vetiver.

The differences in the heavy metal concentrations of vetiver depended on plant tissues, amendment rates, and types of metals (Table 7). Among the tested heavy metals, the maximum concentration was found for Zn in the shoots and roots of vetiver, and the minimum concentration was found for Cd (Table 7), which may have been related to the differences in heavy metal levels in the soils. The concentrations of metals in the tested soils followed a decreasing order: Zn > Pb > Cu > Cd. The concentrations of heavy metals in the roots of vetiver were higher than those in the shoots (Table 7). This result is consistent with Banerjee et al. (2016), who found that concentrations of heavy metals (Pb, Cu, Zn) were higher in the roots than those in the shoots of vetiver growing on mine soils. Thus, vetiver appears to immobilize heavy metals via absorption and accumulation by the roots, implying that vetiver has the potential to stabilize Cd. Pb. Cr. Cu. and Zn.

The concentrations of Cd and Cr in the roots of vetiver were greater with the amendment than with CK (Table 7). The results indicated that the application of amendment increased the phytostabilization of Cd and Cr. This result could

Table 5 Effect of the CaO-activated Si-based slag amendment on plant height, root length (cm), and biomass (g pot⁻¹) of vetiver grown in contaminated soils

Application rate (%)	Plant height (cm)	Root length (cm)	Shoot dry weight (g pot ⁻¹)	Root dry weight (g pot ⁻¹)	Biomass (g pot ⁻¹)
CK	57.73 ± 5.19 a	6.70 ± 2.70 b	1.34 ± 0.39 c	$0.81 \pm 0.57 \text{ b}$	2.14 ± 0.92 c
0.5	41.00 ± 5.66 c	12.50 ± 5.66 a	$3.05 \pm 0.08 \ b$	2.14 ± 0.05 a	$5.20 \pm 0.06 \ ab$
1.0	$49.50 \pm 6.36 \ b$	$8.50\pm1.41~ab$	$3.89 \pm 0.45 \ a$	1.75 ± 0.26 a	$5.65 \pm 0.71 \ a$
2.0	$20.00 \pm 0.00 \ d$	$8.15 \pm 0.21 \ ab$	$3.35 \pm 0.27 \ ab$	$0.93 \pm 0.07 \ b$	$4.29 \pm 0.34 \ b$

CK = control: 0.5 = 0.5% amendment; 1.0 = 1.0% amendment; 2.0 = 2.0% amendment. Means followed by different letters within columns are significantly different (p < 0.05)



Table 6 Effect of the CaO-activated Si-based slag amendment on the concentrations (mg kg⁻¹) of Si in vetiver grown in contaminated soils

Application rate (%)	Shoot	Root
CK	524.48 ± 152.69 a	580.47 ± 292.49 c
0.5	354.70 ± 21.15 ab	$846.78 \pm 13.66 \ bc$
1.0	$360.88 \pm 76.90 \text{ ab}$	$962.60 \pm 147.35 \text{ ab}$
2.0	$310.37 \pm 39.90 \ b$	1244.46 ± 133.39 a

CK = control: 0.5 = 0.5% amendment; 1.0 = 1.0% amendment; 2.0 = 2.0% amendment. Means followed by different letters within columns are significantly different (p < 0.05)

be ascribed to the amendment-induced increase in the absorption and accumulation by roots.

The concentrations of Zn in the roots of vetiver were lower with the amendment than with CK (Table 7), which may have been related to the amendment's ability to stabilize Zn in soils (Table 4). Furthermore, the dilution of Zn due to the increased root dry weight under the application of amendment (Table 5) may also contribute to the decreased Zn levels in the roots.

The application of amendment at low rates (0.5% for Cu, 0.5% and 1.0% for Pb) resulted in decreased concentrations of Cu and Pb in the roots of vetiver (Table 7). This result may be related to the dilution of Cu and Pb caused by the increase in root dry weight under the application of amendment. However, applying the amendment at a high level (2.0%) resulted in increased concentrations of Cu and Pb in the roots (Table 7). This result may be related to the absorption and accumulation of Cu and Pb by the roots. Furthermore, the increased DTPA-extractable Cu in soils and soil pore water Cu with the amendment may have contributed to the increased Cu in the roots (Tables 2 and 4). Similar increases in Cu concentrations in the roots of vetiver were observed under the application of manure compost and sewage sludge containing Cu (Chiu et al. 2006).

The concentrations of Cd, Cu, Pb, and Zn in the shoots of vetiver were lower with the amendment than with CK

(Table 7), which may have been related to an amendment-induced decrease in available Cd and Pb in soils (Table 4). Furthermore, the greater biomass observed with the amendment could have led to a dilution of Cd, Cu, Pb, and Zn in the shoots (Table 5). In addition, an increase in Si due to the application of amendment could inhibit the transport of Cd, Cu, Pb, and Zn from the roots to shoots. The concentrations of Cd in the roots tended to increase as the Si in the roots increased, whereas the concentrations of Cd in the shoots tended to decrease as the Si in the roots increased (Table 6).

Application of an amendment rate of 0.5% led to the lowest concentration of Cd in the shoots of vetiver, whereas a rate of 1.0% led to the lowest concentration of Cu, and 2.0% led to the lowest concentration of Pb and Zn (Table 7). The optimal amendment rate for controlling Pb and Zn concentrations in the shoots was 2.0%, which was higher than that for controlling Cd and Cu (Table 7). This phenomenon could be explained by the difference in the total and available amounts of these metals in soil because their levels followed the decreasing order: Zn > Pb > Cd. The formation of organic-Cu complexes and silicate precipitation on root surfaces could be responsible for the Cu accumulation in the shoots.

The concentrations of Cr in the shoots of vetiver were greater with the amendment than with CK and increased along with the application rate (Table 7), which may have been related to the amendment increasing the soil pH and subsequently enhancing the uptake of Cr. A similar result was observed in the roots of vetiver (Table 7). Hattab et al. (2014) observed that a soil pH > 7 favoured the oxidation of Cr(III) to Cr(VI), thereby increasing Cr mobility and the uptake of Cr by the roots.

At an amendment rate of 1.0%, the concentrations of heavy metals in vetiver shoots were reduced by 24.2% for Cd, 58.4% for Cu, 73.0% for Pb, and 41.1% for Zn compared with those under CK treatment (Table 7). Several studies observed that the application of alkaline amendments could reduce the concentrations of heavy metals by plant shoots. Lim et al. (2013) observed that lime-based amendments significantly reduced

Table 7 Effect of the CaO-activated Si-based slag amendment on the concentrations (mg kg⁻¹ DW) of heavy metals in the shoots and roots of vetiver grown in contaminated soils

	Application rate (%)	Cd	Cr	Cu	Pb	Zn
Shoot	CK	1.32 ± 0.21 a	3.10 ± 0.65 b	8.56 ± 2.60 a	3.93 ± 0.87 a	37.24 ± 7.88 a
	0.5	$0.96 \pm 0.15 \ b$	$3.75 \pm 0.31 b$	$5.10 \pm 0.17 \ b$	$1.08 \pm 0.03 \ b$	$24.14 \pm 1.84 \ b$
	1.0	$1.00 \pm 0.11 \ b$	$3.88 \pm 0.25 \ b$	$3.56 \pm 0.95 b$	$1.06 \pm 0.23 \ b$	$21.94 \pm 0.30 b$
	2.0	$1.05 \pm 0.09 \ ab$	4.99 ± 0.57 a	$4.78 \pm 0.93 \ b$	$0.79 \pm 0.11 \ b$	$20.61 \pm 2.67 \ b$
Root	CK	$1.25\pm0.32\ c$	7.05 ± 1.67 c	$21.07\pm1.85\ b$	$6.32 \pm 2.40 \ b$	189.50 ± 11.17 a
	0.5	$2.46 \pm 0.24 \ b$	$13.78 \pm 1.34 \ b$	$16.61 \pm 2.16 b$	$4.48 \pm 0.38 \ bc$	$35.86 \pm 5.12 \text{ b}$
	1.0	$3.06 \pm 0.53 \ ab$	$9.58 \pm 1.38 \ c$	$22.29 \pm 3.89 \ b$	$3.48 \pm 0.03 \ c$	$31.10 \pm 5.21 b$
	2.0	3.64 ± 0.08 a	$20.00\pm1.32~a$	49.99 ± 5.70 a	16.22 ± 1.43 a	$38.06 \pm 2.47 \ b$

CK = control: 0.5 = 0.5% amendment; 1.0 = 1.0% amendment; 2.0 = 2.0% amendment. Means followed by different letters in each column within the shoot or root category are significantly different (p < 0.05)



the concentrations of Cd (63.99-77.29%) and Pb (47.34-75.95%) in maize shoots. The price of slag amendment is approximately 65 USD t^{-1} , and the cost of amendment for remediation is 1462.5 USD ha^{-1} based on 1.0% amendment $(w/w soil) (22.5 t ha^{-1})$.

The effects of Si on metal accumulation were dependent on the types of metals. Significantly positive correlations were observed between the Si concentration in the pore water and the Cd, Cu, and Pb concentrations in the roots, whereas negative correlations were observed between the Si concentration in the pore water and the Cd, Cu, and Pb concentrations in the shoots (Table 8). This effect could be ascribed to Si depositing with Cd, Cu, and Pb in the root endodermis, which simultaneously physically blocked the apoplast bypass flow across the roots. Gu et al. (2011) reported that Si enhanced the ability of roots to deactivate excess metals by binding them to the cell wall, thereby inhibiting the translocation of metals from roots to shoots. The concentration of Si in the pore water was negatively correlated with the concentration of Zn in the shoots and roots of vetiver (Table 8). The present results suggest that the precipitation of Si with Zn slowed the transfer of Zn from the soil to the roots of vetiver. The formation of phyllosilicate-like precipitates with Zn reportedly enhances the stability of Zn in soils (Gu et al. 2011). Therefore, Si is crucial for alleviating the toxicity of Cd, Cu, Pb, and Zn in vetiver. However, the concentration of Si in pore water positively correlated with the concentration of Cr in the shoots and roots of vetiver (Table 8), which suggested that the amendment increased the Cr uptake in vetiver due to the amendmentinduced increase in soil pH. This phenomenon might indicate that Si-mediated alleviation of Cr phytotoxicity is caused by Simediated detoxification of Cr in vetiver (Adrees et al. 2015).

In summary, our results confirmed that the applied amendment had obvious regulatory effects on the accumulation of Cd, Cr, Pb, Cu, and Zn in vetiver. The application of amendment enhanced the stabilization of heavy metals in soils due to precipitation and adsorption in the soil and root surface.

Effect of the slag amendment on the translocation and bioaccumulation of heavy metals in vetiver

A plant's ability to translocate heavy metals from the roots to shoots is determined by their TF (Mohamed et al. 2015). In the

Table 8 Pearson correlation coefficients between the concentration of Si in the soil pore water and the concentration of heavy metals in the vetiver (n = 12)

	Cd	Cr	Cu	Pb	Zn
Shoot	-0.473	0.858**	-0.548	-0.761**	-0.726**
Root	0.884**	0.873**	0.770**	0.697**	-0.723**

^{*, **}Significant at p < 0.05 and p < 0.01, respectively (two-tailed)

present study, the TF value for Cd was > 1; however, the TF values for other elements (Pb, Cr, Cu, Zn) were < 1 when vetiver was grown in contaminated soils under CK treatment, and the TF values followed the decreasing order Cd > Pb > Cr > Cu > Zn (Table 9). These results are consistent with previous research (Abaga et al. 2014), which found higher TF values for Cd than for Cu in vetiver. This result indicated that vetiver was effective in translocating Cd from the roots to shoots, which is useful for the phytoextraction of Cd. Moreover, most of the extracted Pb, Cr, Cu, and Zn was retained in the roots via precipitation and absorption (Banerjee et al. 2016). Therefore, the restriction of metal translocation from roots to shoots is the mechanism underlying metal tolerance in vetiver (Gautam and Agrawal 2017).

The amendment significantly reduced the TF values for Cd, Cr, Cu, and Pb, and the lowest TF values for Cd, Cr, Cu, and Pb were observed with the application rate of 2.0% (Table 9). This finding may have been related to the amendment-induced increase in the absorption and accumulation of these metals in the roots and precipitation onto the root surface, thereby inhibiting transportation of the metals from the roots to the shoots (Aibibu et al. 2010).

The amendment increased the TF value for Zn, with the highest TF value observed at a rate of 1.0% (Table 9). This finding could be explained by the decreased uptake of Zn in roots (Table 7) due to the application of the amendment increasing the stabilization of Zn in soils (Table 4). A similar result was obtained in vetiver for the phytoremediation of fly ash-contaminated soils (Ghosh et al. 2015).

A plant with a BCF value > 1 indicates that it effectively takes up metal from the soil, whereas a plant with a BCF value < 1 implies that it is a metal excluder (Radziemska et al. 2017). In the present study, the BCF values for Cu and Zn in roots exceeded 1 when vetiver was grown in the contaminated soils under CK treatment, whereas the BCF values for Cd, Cr, and Pb in the roots were less than 1 (Table 9), which may have been related to differences in heavy metal levels in the selected soils. Moreover, our results revealed the high capacity of vetiver to absorb soil Cu and Zn. The BCF values for Cd, Cr, Cu, Pb, and Zn in the shoots were less than 1, which indicated that vetiver showed poor translocation of metals from the soil to its aboveground components.

Application of amendment tended to increase the BCF of Cd and Cr but decrease the BCF of Zn in the roots (Table 9). These results suggest that the application of amendment promoted the transfer of Cd and Cr from the soil to the plant but inhibited the transfer of Zn from the soil. An application rate of 2.0% increased the BCF values for Cu and Pb in the roots, whereas rates of 0.5% and 1.0% tended to reduce these values (Table 9). Low levels of the amendment decreased Cu and Pb concentrations in the roots through the dilution effect of the larger biomass. However, high levels of the amendment significantly increased the absorption and accumulation of Cu and Pb into the roots.



Table 9 Effect of the CaO-activated Si-based slag amendment on the relative translocation and bioaccumulation of heavy metals in vetiver grown in contaminated soils

	Application rate (%)	Cd	Cr	Cu	Pb	Zn
TF	CK	1.13 ± 0.45 a	0.45 ± 0.09 a	0.41 ± 0.12 a	0.68 ± 0.27 a	0.20 ± 0.05 c
	0.5	$0.40 \pm 0.10 \ b$	$0.27\pm0.00\;b$	0.31 ± 0.05 a	$0.24 \pm 0.02 \ b$	$0.68 \pm 0.09 \text{ ab}$
	1.0	$0.34 \pm 0.09 \ b$	$0.41 \pm 0.09 \ a$	$0.17 \pm 0.07 \ b$	$0.31 \pm 0.07 \ b$	0.72 ± 0.13 a
	2.0	$0.29 \pm 0.03 \ b$	$0.25 \pm 0.05 \ b$	$0.10 \pm 0.03 \ b$	$0.05 \pm 0.01 \ b$	$0.54 \pm 0.04 \ b$
BCF-shoot	CK	0.71 ± 0.13 a	0.03 ± 0.01 a	0.48 ± 0.11 a	0.03 ± 0.01 a	$0.51\pm0.07~a$
	0.5	0.60 ± 0.11 a	0.03 ± 0.01 a	$0.23 \pm 0.01 \ b$	$0.01\pm0.00\;b$	$0.31\pm0.03\ b$
	1.0	$0.64 \pm 0.05 \text{ a}$	0.04 ± 0.00 a	$0.15 \pm 0.02 \ b$	$0.01\pm0.00\;b$	$0.30 \pm 0.02 \ b$
	2.0	0.60 ± 0.06 a	0.04 ± 0.01 a	$0.14 \pm 0.04 b$	$0.01\pm0.00\;b$	$0.24\pm0.02\ b$
BCF-root	CK	$0.66 \pm 0.15 c$	$0.07 \pm 0.02 \ d$	$1.20 \pm 0.10 b$	$0.06 \pm 0.02 \ b$	2.67 ± 0.43 a
	0.5	$1.52 \pm 0.10 \text{ b}$	$0.13 \pm 0.02 \ b$	$0.75 \pm 0.15 c$	$0.05 \pm 0.00 \ b$	$0.46\pm0.04~b$
	1.0	1.96 ± 0.40 a	$0.10 \pm 0.02 \ c$	$0.97 \pm 0.27 \ bc$	$0.04 \pm 0.00 \ b$	$0.43\pm0.10\;b$
	2.0	2.06 ± 0.06 a	$0.17 \pm 0.01 \ a$	1.49 ± 0.10 a	0.14 ± 0.02 a	$0.45 \pm 0.01 \ b$

CK = control: 0.5 = 0.5% amendment; 1.0 = 1.0% amendment; 2.0 = 2.0% amendment. TF (translocation factor): the ratio of metal concentration in the shoots to that in the roots. BCF-shoot/root: the ratio of the metal concentration in the plant shoot/root to the metal concentration in the soil at harvest. Means followed by different letters in each column within the TF or BCF-shoot/root category are significantly different (p < 0.05)

Application of amendment tended to reduce the BCF values for Cd, Cu, Pb, and Zn in the shoots (Table 9), which was consistent with the findings of previous studies on red mud levels in sludge-amended soil planted with vetiver (Gautam and Agrawal 2017). This phenomenon could be attributed to the decrease in phytoavailable metals due to the increase in soil pH with the application of amendment, which induced a lower rate of transfer of metals from the soil to the shoots of vetiver. Obvious differences in the BCF values for Cr were not observed in the shoots with or without amendment (Table 9). The amendment-induced changes in the BCF values could be concealed because of the high level of Cr in the soil.

Suitability of vetiver for the phytoremediation of heavy metal in soils

Both the TF and BCF are used to assess the phytoremediation potential of heavy metals by plants (Banerjee et al. 2016). Plants with BCF and TF values higher than 1 are suitable for heavy metal phytoextraction. Plants with high BCF and low TF values are suitable for heavy metal phytostabilization (Brandão et al. 2018).

The results of this study demonstrated that vetiver has the ability to perform phytoextraction and phytostabilization based on the composition of heavy metal elements. The results also indicated that vetiver has a higher potential for phytoextraction of Cd and is suitable for phytostabilization of Cu and Zn. Generally, the phytostabilization of heavy metals in vetiver followed a decreasing order of Zn > Cu > Cd > Pb/Cr based on the BCF value of vetiver (Table 9). In terms of revegetation, a lower metal concentration in the

shoots is preferred. Therefore, the use of vetiver is a suitable remediation strategy for soils contaminated with Cr and Pb. The amendment was beneficial for the phytostabilization of all the heavy metals and thus represents a suitable remediation strategy in multi-metal-contaminated soils. An application rate of 1.0% is recommended for use in the studied soils.

Conclusions

The present study confirmed that vetiver could grow in multimetal (Cd, Zn, Cr, Pb, Cu)-contaminated soils, although its growth was obviously inhibited. Vetiver was efficient at transporting Cd from the roots to shoots and phytostabilizing Pb, Cr, Cu, and Zn in the roots. The application of a CaOactivated Si-based slag amendment increased the growth of vetiver, and the highest biomass (2.62 times higher than the control) was obtained at the 1.0% amendment level. The inhibited heavy metal uptake by vetiver under the amendment treatments was likely related to two processes: the immobilization of soil heavy metals due to the alkaline amendmentinduced increase in soil pH and the Si-induced accumulation of heavy metals in the roots of vetiver. Therefore, vetiver represents an excellent candidate for the remediation and restoration of multi-metal-contaminated soils in combination with the application of CaO-activated Si-based slag amendment. Further investigations are required to determine the feasibility of remediating and restoring multi-metalcontaminated soils at the field scale.

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