Water Air Soil Pollut (2014) 225:2194
DOI 10.1007/s11270-014-2194-4

Remediation of Cd, Pb, and Cu-Contaminated Agricultural Soil Using Three Modified Industrial By-products

Peng Yin · Lin Shi

Received: 15 July 2014 / Accepted: 16 October 2014 / Published online: 29 October 2014

Abstract In this study, the potential effects of three modified industrial by-products—modified low-grade phosphate rock with soda dregs (MP), modified flue gasses desulfurization residue (MF), and a mixture of MF and phosphoric acid (MFP)—were evaluated in the remediation of heavy metal-contaminated agricultural soil at four different treatment levels. The effects of the amendments on the extractability and phytoavailability of soil heavy metals were tested using a standardized sequential extraction test and a pakchoi pot experiment. The impacts of the three amendments on soil quality was investigated, including changes of soil pH, availability of K, Ca, Mg, Si and P, and the effects on pakchoi growth. The addition of these amendments resulted in a significant decrease of labile fraction of the heavy metals in soil ($p<0.05$) and a marked decrease in heavy metal uptake by pakchoi ($p<0.05$) in the pot experiment. All the amendments improved soil quality as measured by neutralization of soil acidity, increased content of mineral nutrients of soil (specifically, available K, Ca, Mg, Si, and/or P), and enhanced pakchoi growth when compared to the controls. Significant correlations (positive/negative) were observed among these factors, indicating multiple effects of the amendments on the remediation process. The increased soil pH and elevated mineral nutrients contributed to the stabilization of heavy metals, and the remediated soil conditions resulted in improved growth of pakchoi. These results suggest that all three of the modified industrial by-products could be used for the remediation and restoration of heavy metal-contaminated agricultural soil.

Keywords Remediation · Heavy metals immobilization · Modified industrial by-products · Contaminated agricultural soil · Soil quality

1 Introduction

Heavy metal-contaminated soil is a worldwide problem that urgently needs to be solved, especially in China where more than 10 % of farmlands have been contaminated by heavy metals and no fewer than 11 provinces have been affected, especially south of the Yangtze River (Tencent 2012). According to data from the Bulletin of Soil Pollution Situation Investigation of People's Republic of China (MEPC 2014), agricultural soil has been polluted mainly due to anthropomorphic activities (such as industry, mining, and agriculture) and has

---

P. Yin · L. Shi
College of Environment and Energy, South China University of Technology, Guangzhou 510006, People's Republic of China

P. Yin · L. Shi
Guangdong Provincial Key Laboratory of Atmospheric Environment and Pollution Control, South China University of Technology, Guangzhou 510006, People's Republic of China
e-mail: celshi@126.com

P. Yin · L. Shi (✉)
The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, South China University of Technology, Guangzhou 510006, People's Republic of China
e-mail: celshi@126.com

resulted in soil levels above the standard for Cd, Pb, and Cu in 7.0, 1.5, and 2.1 % of the cases, respectively. Unlike organic contaminants, heavy metals in soil are non-biodegradable and, therefore, persist in soil for a long time, leading to long-term (chronic) effects on the soil environment (Bolan et al. 2003). Heavy metals in soil can threat people's health either by accidental soil ingestion, by breathing contaminated soil dust particles or by the ingestion of polluted drinking water or farm products associated with contaminated soil. Therefore, it is necessary to implement appropriate soil remediation practices to reduce the bioavailability of metals in soils in order to protect human health.

Conventional soil-remediation technologies, such as excavation, transport, soil replacement, and landfilling of contaminated soil, are effective, but may be too expensive for the remediation of large areas of contaminated agriculture fields. The agricultural-based approach of in situ stabilization by applying soil amendments was recognized as a realistic choice in the case of vast contaminated farmlands (Mulligan et al. 2001). While in situ stabilization treatments do not reduce heavy metal concentrations in soil, they do enhance the soil mechanisms that controlling heavy metal mobility and bioavailability. It has been reported that the addition of various amendments (e.g., lime, hydroxyapatite, silicon materials) to soil decreased the mobility and bioavailability of heavy metals and reduced their toxic potential (Bolan et al. 2003; Vieira da Cunha and Araujo do Nascimento 2009; Padmavathiamma and Li 2010).

In recent years, many studies have focused on using industrial wastes and by-products as amendments in order to remediate the soil and, at the same time, putting these materials to good use. A number of materials, such as red mud, steel shot, furnace slag, sugarbeet lime, and flue gasses desulfurization (FGD) residue (Friesl et al. 2004; Garrido et al. 2005; Lee et al. 2011a) have been used, and the remediation effects have varied depending on the particular metals, soil properties, and experimental conditions. Usually, the industrial wastes applied as amendments were simply ground up or sieved, at best before use and lacked any specific processing designed to achieve better remediation results. These materials did not reduce heavy metal toxicity efficiently, and sometimes, large doses were needed to achieve the desired level of remediation (Stehouwer et al. 1995; Lee et al. 2011a; Ahmad et al. 2012), which often had negative influences on soil properties, such as compaction, overliming and basification. On the other hand, the amendments can enhance the amount of some mineral nutrients (K, Ca, Mg, Si, and/or P) that contribute to the restoration of contaminated farmland. Only a few studies have reported on the effects of the added mineral nutrients on the mitigation of toxic heavy metals and their effect on plant growth.

In this work, three modified industrial by-products (modified low-grade phosphate rock (MP), modified flue gasses desulfurization (MF), and a mixture of MF and phosphoric acid (MFP)) were applied to heavy metal-contaminated soil collected from a farmland near a copper and iron mine. The specific objectives were to (i) examine the efficiency of the three modified industrial by-products on heavy metals stabilization in polluted soil; (ii) estimate the effects of the amendments on the improvement of soil quality (acidity amelioration and increase in mineral nutrients) and plant growth; and (iii) analyze the correlations of soil and plant parameters in order to investigate the potential mechanism(s) of reducing heavy metals toxicity.

2 Materials and Methods

2.1 Sampling and Characterization

Top soil (<20 cm depth) was collected from a farmland adjacent to Dabaoshan copper and iron mine, Shaoguan City, Guangdong province, People's Republic of China (24.47 N, 113.8 E). The soil sample was air-dried and sieved at <2 mm in preparation for determining its physiochemical properties. Soil organic matter (OM) was determined according to the Walkley–Black procedure (Nelson and Sommers 1982). Soil pH was measured using 1:2.5 (by weight) soil:H_2O mixture. Available K, Ca, and Mg in the soil was extracted with 1 M ammonium acetate (Ok et al. 2007) and analyzed using atomic absorption spectrometry (Shimadzu, AA6300C, Japan). For available P, soil was extracted with 0.5 M $NaHCO_3$, and P in the extracts was determined following an ascorbic acid blue color method (Watanabe and Olsen 1965). Soil available silicon was tested by the method of Acquaye and Tinsley (1965).

The digestion of soil samples was performed using the HNO_3, HF, and $HClO_4$ hot block digestion procedure, and heavy metals were measured by graphite furnace atomic absorption spectrometry (GFAAS) (Shimadzu, AA6300C, Japan). Some properties of the soil are presented in Table 1.

Table 1 Basic properties of the studied soil (mean values of three replicates)

pH	Organic matter (%)	Available (mg/kg)					Total[a] (mg/kg)			
		P	K	Ca	Mg	Si	Cd	Pb	Cu	Cr
3.83	2.41	77.2	241.6	743	63.03	64.04	0.4 (0.3)[b]	257 (250)	225 (50.0)	47.9 (250)

[a] Total Cd, Pb, Cu, and Cr concentrations in soil sample

[b] Numbers in parenthesis are values specified by "Chinese Environmental quality standard for soils" (GB 15618–1995)

2.2 Soil Amendments

The amendments used in this experiment were three modified industrial by-products. The first amendment was a modified low-grade phosphate rock (MP), prepared by calcining a mixture of low-grade phosphate rock and soda dregs at an appropriate ratio. The low-grade phosphate rock was collected from a phosphate ore-dressing plant in Zhanjiang, People's Republic of China, and the soda dregs, discharged from the ammonia-soda process, were derived from the South China Soda Ash Manufacturing Co., Ltd, Guangzhou, People's Republic of China. The low-grade phosphate rock and soda dregs were finely ground and sieved before being mixed in an appropriate $P_2O_5/CaSO_4$ molar ratio. Then, the mixture of the two industrial by-products was calcined for 1 h at 1000 °C to activate the inactive apatite and SiO_2 in the low-grade phosphate rock. A nutrient amendment with available P, Si, Ca, and Mg was obtained with the above process.

The second amendment was a modified flue gasses desulfurization residue (MF) prepared by calcining a mixture of FGD residue and potassium feldspar. The preparation process has been reported in detail by Shi et al. (2011). The FGD residue and potassium feldspar were finely ground and mixed together based on the ratios in the following equation:

$$2KAlSi_3O_8 + CaSO_3 + 14CaCO_3 = K_2SO_4 + Ca_3Al_2O_6 + 6Ca_2SiO_4 + 14CO_2$$

The mixture of the two materials was calcined for 1 h at a temperature of 1000 °C in a rotary furnace, resulting in an amendment with available K, Ca, Si, and Mg. The third amendment (MFP) was prepared as a mixture of phosphoric acid and MF at 5 % (*w/w*). This material could provide P in the amelioration process which was absent in the MF treatment alone. Some properties of the amendments are given in Table 2.

2.3 Experiment Setup

The amendments were applied to soils at doses of 0.5, 1, 2, and 4‰ by weight and thoroughly mixed with the soil to obtain homogeneity. Non-amended soils were used as a control group. Then, the soils were placed plastic pots (3 kg capacity, 19 cm diameter, and 17 cm height, three replicates per treatment). Twenty pakchoi seeds were sown in each pot, which were culled to five plants 2 weeks after germination. Soil moisture was maintained at 75 % field capacity by adding water to compensate for water loss. The experiment was conducted under controlled conditions (temperature 20–30 °C, relative humidity 60–70 %) with daily watering.

Table 2 Characterizations of the amendments (mean values and standard deviations of three replicates)

Parameter	MF	MFP	MP
pH[a]	12.31±0.04	11.66±0.02	9.420±0.07
Available K_2O (%)[b]	4.42±0.040	4.36±0.060	0.29±0.004
Available CaO (%)	35.54±0.41	31.66±0.40	45.87±0.39
Available MgO (%)	5.76±0.045	5.19±0.015	2.23±0.17
Available SiO_2 (%)	20.03±1.57	21.40±1.23	13.77±0.741
Available P_2O_5 (%)	0.513±0.072	4.02±0.34	11.1±0.044
Cd (mg kg^{-1})[c]	0.11±0.02	0.12±0.01	0.12±0.007
Pb (mg kg^{-1})	14.5±1.32	15.9±1.24	5.73±0.752
Cu (mg kg^{-1})	11.0±0.93	11.9±0.21	12.0±0.67

MP modified low-grade phosphate rock, *MF* modified flue gasses desulfurization residue, *MFP* MF + phosphoric acid

[a] Amendment pH measured at the ration of solid to H_2O as 1:2.5 (mass:volume)

[b] Available K, Ca, Mg, Si, and P in amendments were determined followed by Chinese agriculture standards: NY/T 2272–2012 and NY/T 2273–2012

[c] Total concentrations of Cd, Pb, and Cu in the amendments

2.4 Plant Analysis

After 6 weeks, pakchoi was harvested with shoot (leaves) separated from root. The growth of pakchoi in each treatment was evaluated by measuring shoot height and, shoot and root mass. After being washed thoroughly with deionized water, the leaves and roots were dried at 70 °C for 48 h. The digestion of plant tissues was performed using the HNO_3/H_2O_2 hot block digestion procedure (EPA 1986). Heavy metals (Cd, Pb, and Cu) in the digested solutions were determined using GFAAS (Shimadzu, AA6300C, Japan).

2.5 Five-Step Sequential Extraction

Changes of the fractions of heavy metals were determined using the procedure described by Tessier et al. (1979). Heavy metals were separated into five operationally defined fractions. First, a soil sample was extracted with 8 mL 1 M NaOAc at pH 8.2 for 1 h, producing F1, the exchangeable fraction. Second, the fraction bound to soil carbonates was extracted from the residue of first step with 1 M NaOAc at pH 5, producing F2, the carbonate-bound fraction. Third, the fraction bound to Fe and Mn oxides was extracted with 0.04 M hydroxylamine hydrochloride in 25 % (*v/v*) HOAc, producing F3, the Fe-Mn oxide fraction. Fourth, the fraction bound to organic matter was obtained after heating the soil residue from the previous step in 0.02 M HNO_3 and 30 % H_2O_2 for 3 h, followed by extraction with 3.2 M NH_4OAc for 30 min, producing F4, the fraction bound to organic matter. The fifth and final residual fraction was obtained by digesting the residual of soil samples with HF-$HClO_4$, producing F5, the residual fraction. Heavy metals in the extraction solutions were determined with GFAAS (Shimadzu, AA6300C, Japan).

2.6 Statistical Analysis

All the data were statistically analyzed using one-way ANOVA at a significance level of $P<0.05$ (marked by * in this paper) and $P<0.01$(marked by ** in this paper) with SPSS 17.0 software$^{@}$. The Duncan test was used to detect the significant differences between the means of the different treatments.

3 Results and Discussion

3.1 Effect of the Amendments on Soil pH

Figure 1 presents the change of soil pH after being amended with MP, MF, and MFP. Owing to the strong alkalinity of the amendments (Table 2), soil pH increased by 0.13–0.88 units with MP, 0.32–1.26 units with MF and 0.11–1.16 units with MFP when compared with the control. The increase of soil pH was consistent with the increasing rates of amendments applied.

Unreacted CaO, MgO, and new substances of the amendments, such as $MgSiO_3$, $Ca_2MgSi_2O_7$, $CaMgSiO_4$, and some other amorphous Ca and/or Mg compounds, may react with H^+ ions in the soil solution (pH=3.83) which increased the soil pH directly. In this study, pH showed significantly positive correlations with available Ca and Mg (r=0.776** and 0.862**, respectively) which were similar to the findings of Ok, who found that increased available Ca led to the release of OH^- ions in the soil solution (Ok et al. 2011). Also, increased availability of Ca^{2+} and Mg^{2+} in the amended soil (Table 3) reduced the exchangeable acidity (Noble and Hurney 2000), which improved soil resistance to acidification.

3.2 Effect of the Amendments on Mineral Nutrients in Soil

As presented in Table 3, almost all of the three amendments resulted in improvement of available mineral nutrients; i.e., K, Ca, Mg, Si and/or P.

In the MP treatments, available K decreased significantly compared to the control (Table 3), possibly due to the better growth of pakchoi (Fig. 7) which assimilated much more K than the control but without extra K to replenish the adsorption loss (Table 2). In contrast, for the MF and MFP treatments, since the MF and MFP could provide adequate K that the pakchoi needed (Table 2), especially in the 2 and 4‰ mixtures, soil available K increased significantly ($p<0.05$) compared to the control. As all the amendments are rich in available Ca, Mg and Si, especially MF and MFP, the addition of the amendments increased soil Ca, Mg, and Si content as a whole and the increase reached statistical significance ($p<0.05$) in the 2 and 4‰ mixtures. The application of P-rich amendment (MP) enhanced soil available P significantly ($p<0.05$), but

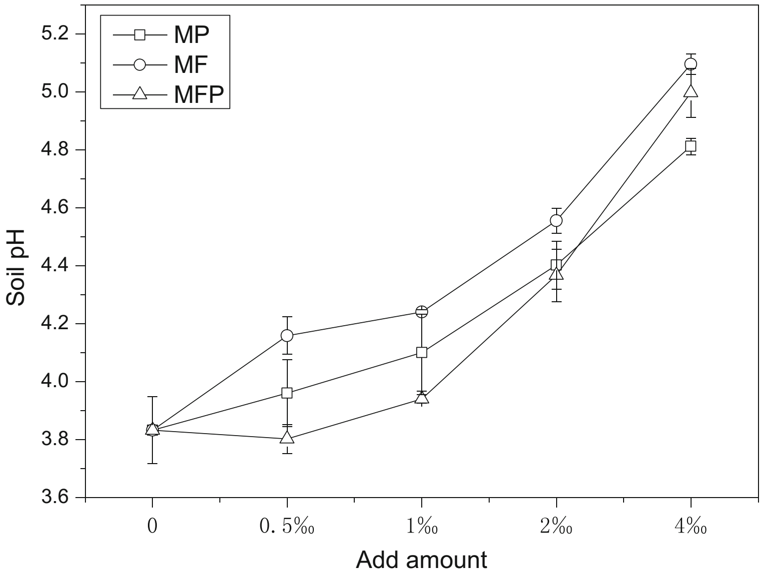

Fig. 1 Effect of the amendments on soil pH

there were no significant differences observed among MF treatments which could provide less available P (Table 2). Although the MFP treatment increased soil available P, the increases did not reach significant level. These findings indicate that soil nutrients status was improved in response to the application of the amendments.

3.3 Effect of the Amendments on Heavy Metal Distribution: Sequential Extraction

In this study, sequential extraction was used to investigate the distribution of metals among different soil pools. The relative distributions of Cd, Pb, and Cu in untreated and amended soils are shown

Table 3 Effect of amendments on mineral nutrients of soil

Treatments	K (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	Si (mg/kg)	P (mg/kg)
MP-amended soil					
0	241.76a	743.53c	63.031d	64.04c	77.28c
0.5‰	214.34b	502.62e	109.96b	66.99c	86.53bc
1‰	214.56b	608.91d	86.613c	64.77c	103.7ab
2‰	200.02b	833.77b	117.41b	83.97b	102.4ab
4‰	209.35b	1190.9a	140.66a	114.3a	116.7a
MF-amended soil					
0	241.76b	743.53c	63.031e	64.04c	77.28b
0.5‰	208.72c	413.66e	98.632d	62.56c	79.84b
1‰	238.41b	522.26d	176.54c	69.21c	91.1a
2‰	262.84a	812.86b	194.76b	99.48b	79.3b
4‰	274.13a	971.51a	226.85a	162.3a	74.9b
MFP-amended soil					
0	241.75c	743.53c	63.031e	64.04d	77.28a
0.5‰	240.75c	624.48d	73.594d	65.51cd	88.31a
1‰	248.95c	724.29c	101.56c	72.16c	85.23a
2‰	275.6b	918.95b	126.29b	89.15b	82.66a
4‰	305.89a	1320.8a	199.81a	166.7a	81.92a

Means (n=3) followed by different letters within a column are significantly different (P<0.05) in Figs. 2, 3, and 4. The first two fractions, namely the exchangeable fraction (F1) and the carbonate fraction (F2), are considerably more labile or mobilizable, and also more easily bioavailable, thereby posing greater risks to the environment and human health (Tessier et al. 1979; Lee et al. 2011b). Initially, Cd existed in a more available/mobile form than the other two metals, with 40 % of total Cd in the exchangeable and carbonate-bound fractions (F1–F2), whereas Pb and Cu in the non-amended soil were mainly in the residual fraction (F5) (64.2 and 52.0 % of total content, respectively), with relative levels in the low mobile fractions (F1–F2, 6.8 and 4.9 % of total content, respectively). After the amendments, heavy metals were found less in the mobile/available (F1–F2) fractions and more in the stable/residual (F3–F5) fractions.

The addition of the three amendments decreased the F1 fraction of Cd markedly with the largest reductions (13.6, 31.9, and 29.6 %) being reached in the 4‰ MP, MF, and MFP treatments, respectively (Fig. 2). The level in the F1 was mainly shifted to F3 fraction which increased 18.9, 15.0, and 26.9 % in 4‰ MP, MF, and MFP treatments, respectively. However, the F5 fraction of Cd decreased 13.5–24.8 % and 20.8–28.0 % in MP and MFP treatments.

Figure 3 shows that the amendments mainly shifted Pb from the F1 fraction to the F3 and F4 fractions. Significant changes were observed in the 4‰ MP, MF, and MFP treatments, where the exchangeable (F1) fraction decreased 56.4, 42.5, and 52.4 %, respectively, while the Fe-Mn oxide (F3) fraction increased 8.2, 5.7 and 10.2 %, respectively, and the organic combined (F4) fraction increased 9.8, 8.5, and 9.3 %, respectively.

As in the case of Cd and Pb, the amendments resulted in a shift of Cu from the labile fractions (F1 and F2) to more stable fractions (F3–F4) (Fig. 4). In the 4 % mixtures, the F1 fractions of Cu decreased 29.1 % (MP), 29.8 % (MF), and 34.3 % (MFP), while at the same time, the F3 fraction and/or F4 fractions increased markedly.

The mobility and/or availability of metals in soil can also be assessed on the basis of relative fractions weakly bound to soil components (i.e., F1 + F2). A relative index of metal mobility was calculated as “the mobility factor” (Narwal et al. 1999) using the following equation:

$$\mathrm{M} = \frac{(F1 + F2)}{(F1 + F2 + \mathrm{F3} + \mathrm{F4} + \mathrm{F5})} \times 100$$

where “M” is the relative content of the mobile fraction (F1 + F2). As can be seen in Table 4, initially, the

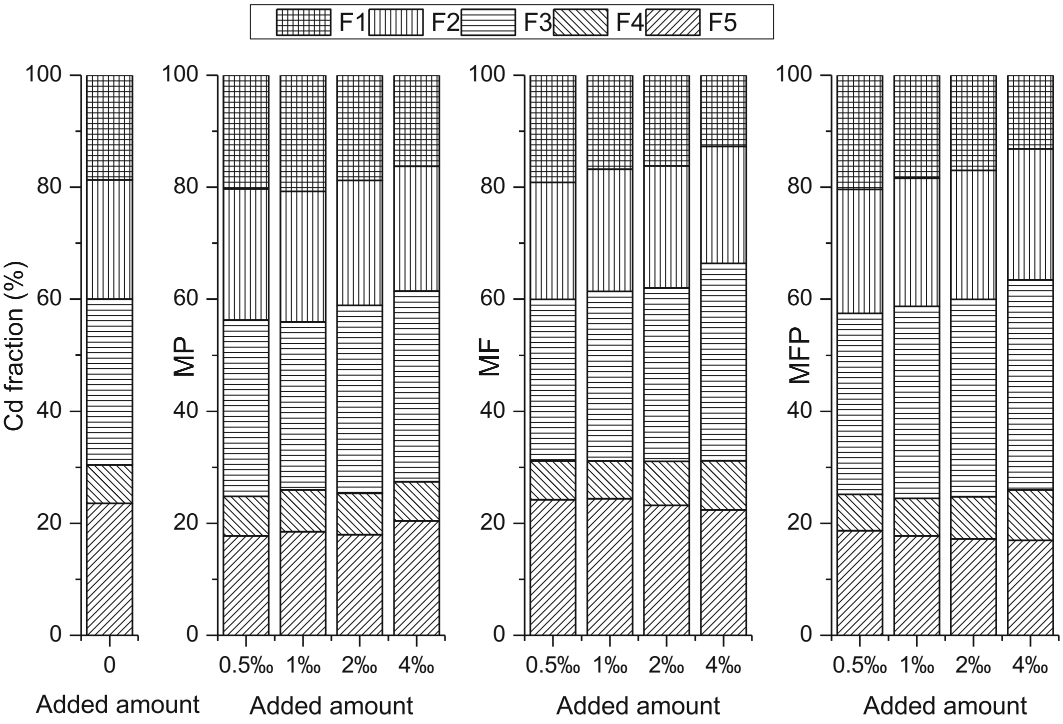

Fig. 2 Distribution of Cd fractions in different amendments addition soils

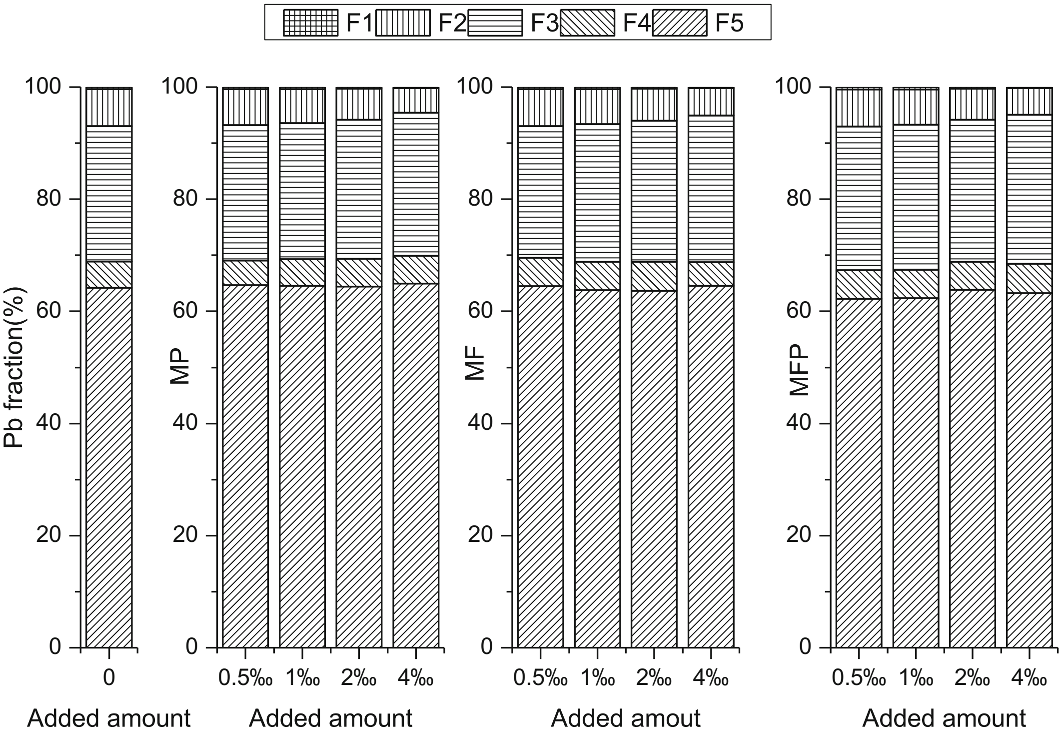

Fig. 3 Distribution of Pb fractions in different amendments addition soils

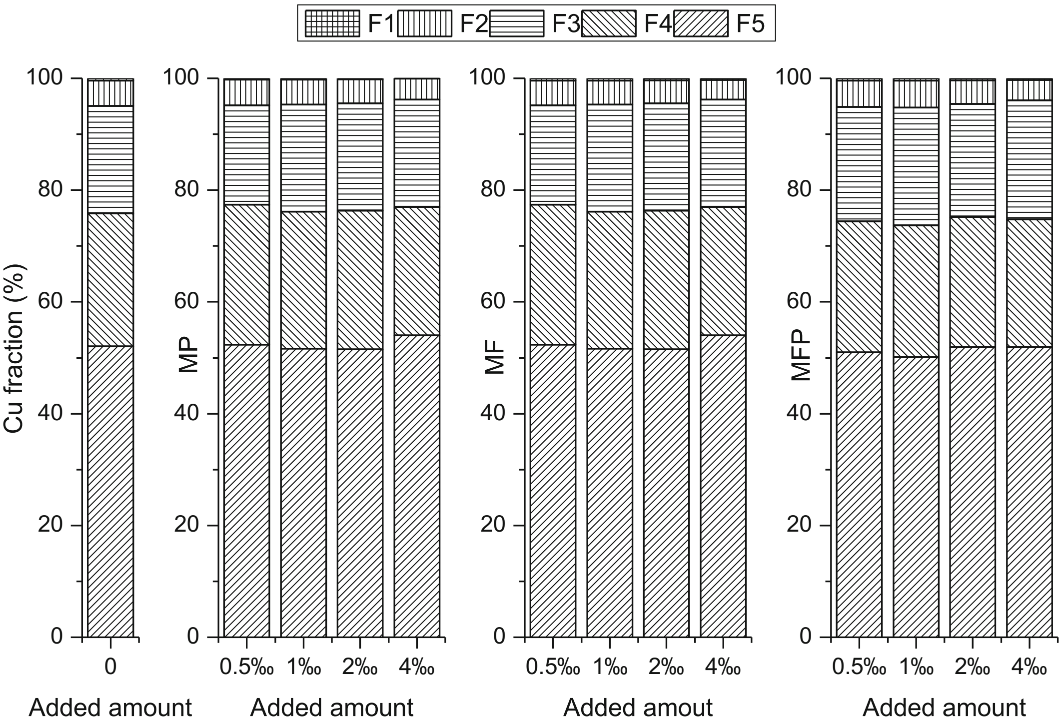

Fig. 4 Distribution of Cu fractions in different amendments addition soils

Table 4 Mobility factor of heavy metals in different amendments addition soils

Treatment		M (%)				M (%)				M (%)		
		Cd	Pb	Cu		Cd	Pb	Cu		Cd	Pb	Cu
0‰	MP	40.3ab	6.93d	4.93c	MF	40.3b	6.93d	4.93d	MFP	40.3b	6.93c	4.93c
0.5‰		43.7bc	6.72d	5.02c		40.4b	6.96d	4.81 cd		42.5b	7.01c	5.14 cd
1‰		44.3c	6.41c	4.85bc		38.6b	6.58c	4.70c		41.3b	6.72c	5.23d
2‰		41.1abc	5.84b	4.68b		37.9b	6.01b	4.45b		40.2b	5.84b	4.55b
4‰		38.5a	4.53a	4.07a		33.6a	5.08a	3.82a		36.5a	4.93a	3.92a

Means followed by same letter with in a column are not significantly different ($P>0.05$)

M mobility factor

mobility factor was 40.3, 6.93, and 4.93 % for Cd, Pb, and Cu, respectively. The amendments decreased the mobility factor of heavy metals significantly ($P<0.05$), with the lowest M value of Cd, Pb, and Cu being observed in 4‰ MF-amended soil, MP-amended soil, and MF-amended soil, respectively (Table 4).

In this study, the application of amendments accelerated the reduction of the labile heavy metal pool (Figs. 2–4, Table 4). Increase of soil pH in these treatments seems to be the main reason for the reduction. A significant negative correlation was got between exchangeable fraction of heavy metals and soil pH values for all the treatments ($r = -0.893^{**}$, -0.965^{**}, and -0.961^{**} for Cd, Pb, and Cu, respectively), indicating that the increase of soil pH duo to the addition of amendments led to the decrease in solubility of Cd, Pb, and Cu. Similar results have been reported in other studies (Janoš et al. 2010; Padmavathiamma and Li 2010; Ahmad et al. 2012).

Soil pH regulates the ionization of pH-dependent exchange sites on organic matter and oxide clay minerals, and the increased pH improved negative surface charge of soil and ionized pH-dependent exchange sites, raising cation-exchange capacity (CEC) and gets much more metals adsorbed on soil particles (Mench et al. 2000; Appel and Ma 2002; Bolan et al. 2003; Hong et al. 2007). What's more, soil pH controls dissolution/precipitation reactions and influences metal speciation in soils (Adriano et al. 2004). Therefore, the increased soil pH converted heavy metal to much more stable fractions.

In addition to increased soil pH, there are other factors that affect the immobilization of Cd in the soil. In MP treatments, the increase in available P of soil may play a role in the retention of Cd, where a negative correlation between available P and exchangeable Cd was found ($r=-0.468$). Cd can be stabilized by co-adsorption of phosphate as an ion pair and surface complex formation of Cd on the phosphate compound in phosphoric amendment remediated soil (Bolan et al. 2003). Typically, stable and insoluble Cd phosphates may be formed due to the elevated available P content in MP-treated soil (Matusik et al. 2008). All three amendments raised the level of available Si in the soil significantly. In addition, a significant negative correlation between available Si and exchangeable Cd was observed; specifically, $r=-0.886^{*}$, -0.956^{*}, and -0.957^{*} for MP, MF, and MFP, respectively. Moreover, much more Cd was found in Fe-Mn oxide-bound fraction in the amended soil compared to non-amended soil (Fig. 2). These results suggest an interaction between Si and Cd, and in fact, previous research has found that Si induced co-precipitation of Cd and Si in soil is a mechanism responsible for the reduction of labile Cd in amended soil (Sarwar et al. 2010).

Besides the increase of soil pH, the retention of Pb in MP treatments could be attributed to the P content of MP, as well. Phosphorus in soil can form stable and low-solubility phosphates with Pb (McGowen et al. 2001) and even generate much more stable substances, such as pyromorphite (Cao et al. 2002; Chen et al. 1997). Successful immobilization of Pb in soil requires sufficient phosphorus to provide free phosphate ions in the soil (Ma et al. 1995). By the addition of phosphate amendment (MP), there was an increase of 11.68–50.65 % available P in the soil (Table 3), thereby facilitating the formation of stable lead phosphates and decreasing the labile fractions of Pb. The significantly negative relationship between labile fraction Pb and available P in MP-amended soil ($r=-0.832^{*}$) confirmed this possibility indirectly. Pb can also be stabilized by being adsorbed on the surface of the phosphate rock particles and fixed by subsequent cation exchange between phosphate rock Ca^{2+} and Pb^{2+} in soil solution (Shashkova et al. 1999). In MF and MFP amended soil, available Si and Ca negatively correlated with exchangeable fraction and the sum of exchangeable nd carbonate bound fractions ($r=-0.934^{**}$ and -0.759^{*}, for F1 fraction and $r=-0.963^{**}$ and -0.886^{*} for F1 + F2, respectively), indicating an interaction between Pb, Ca, and Si. Similar studies have reported that Pb may be immobilized by being entrapped into calcium-silicate-hydrate in amended soil (Badreddine et al. 2004; Cao et al. 2008; Ahmad et al. 2012).

Although the increase of soil pH was the main reason for the reduction of exchangeable Cu (Kumpiene et al. 2008), the decrease of labile Cu can also be ascribed to the precipitation of Cu–phosphate minerals (Garrido et al. 2005). A significant negative correlation between exchangeable Cu and available P in MP-amended soil ($r=-0.947^{*}$) supports this possibility indirectly; furthermore, a similar result was reported by Garrido et al. (2005). In addition, the retention of Cu in this study may reflect the precipitation of Cu oxy-hydroxides and formation of complexes on the surface of Al oxy-hydroxides (Garrido et al. 2005).

3.4 Effect of the Amendments on the Phytoavailability of Heavy Metals

The application MP, MF, and MFP significantly decreased the concentrations of heavy metals in the shoot of pakchoi, except for the 0.5‰ MFP treatment for shoot Pb (Fig. 5). Compared with non-amended

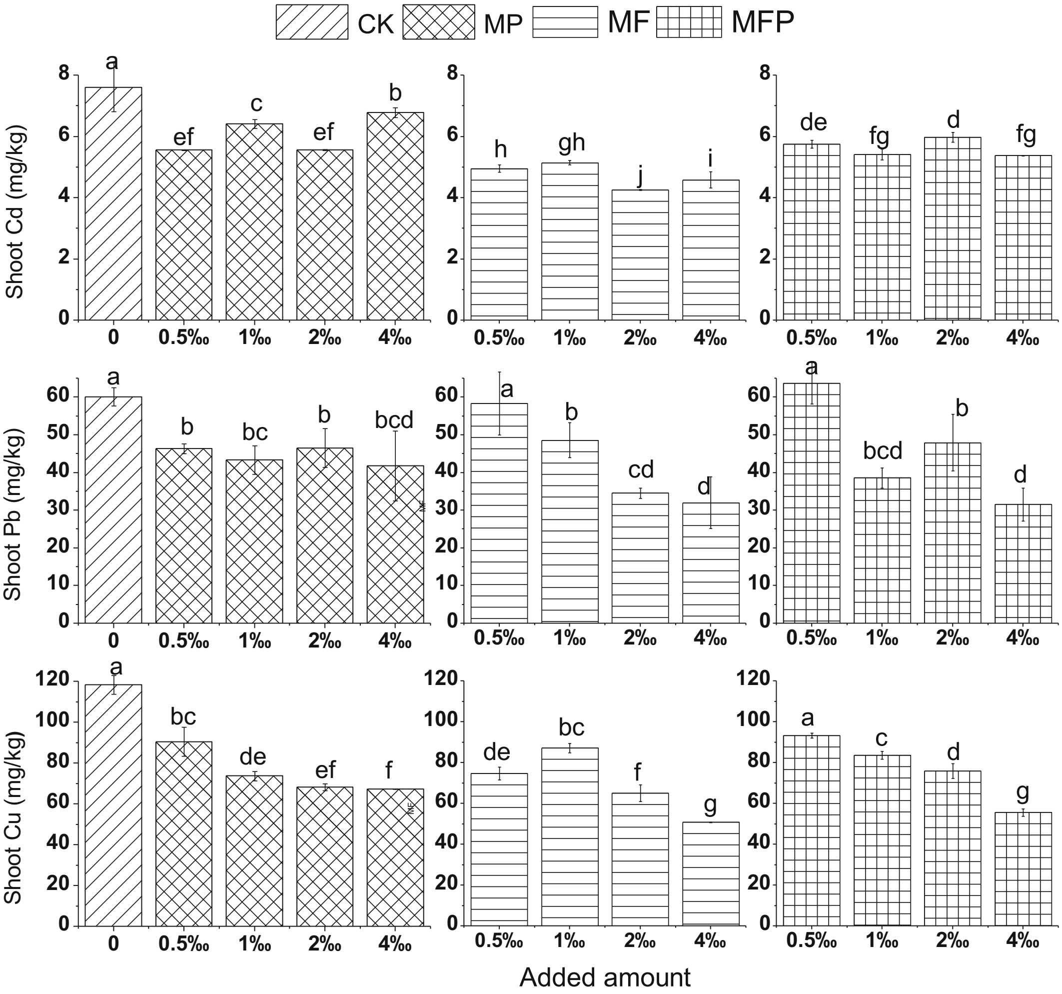

Fig. 5 Concentrations of Cd, Pb, and Cu in the shoot of pakchoi in different treatments (different letters identify the significant difference ($P<0.05$) among treatments)

treatments, all the amended treatments decreased the Cd, Pb, and Cu in the shoot of pakchoi by 10.83–43.92 %, 2.87–47.5 %, and 21.14–57.07 % of, respectively. The lowest Cd, Pb, and Cu concentrations in pakchoi shoot were observed in 2‰ MF-amended treatment, 4‰ MFP-amended treatment, and 4‰ MF-amended treatment, respectively.

Similar to the reduction of heavy metals in the shoot, the concentrations of heavy metals in the plant root were significantly reduced by the addition of amendments (Fig. 6). Compared with the control group, the addition of amendments reduced the Cd, Pb, and Cu in the root of pakchoi by 2.35–39.3 %, 46.14–84.51 %, and 32.63–79.26 %, respectively. The largest reduction of Cd was observed in 2‰ MF-amended soil, and the lowest Pb and Cu were both observed in 4‰ MFP-amended soil.

The decreased phytoavailability of heavy metals can be attributed to the redistribution of metal species (from mobile and/or available fractions to stable and/or unavailable fractions) by the addition of amendments (Figs. 2, 3, and 4 and Table 4), which reduced heavy metal uptake by pakchoi directly. The significantly positive correlation between the concentrations of heavy metals in the F1 fraction and the heavy metals the plant absorbed indicate this possibility indirectly (r=0.369/0.689**, 0.629*/0.513, and 0. 851**/0.872** for shoot/root Cd, Pb, and Cu, respectively). Lee et al. (2011a) also found that the correlation coefficients were

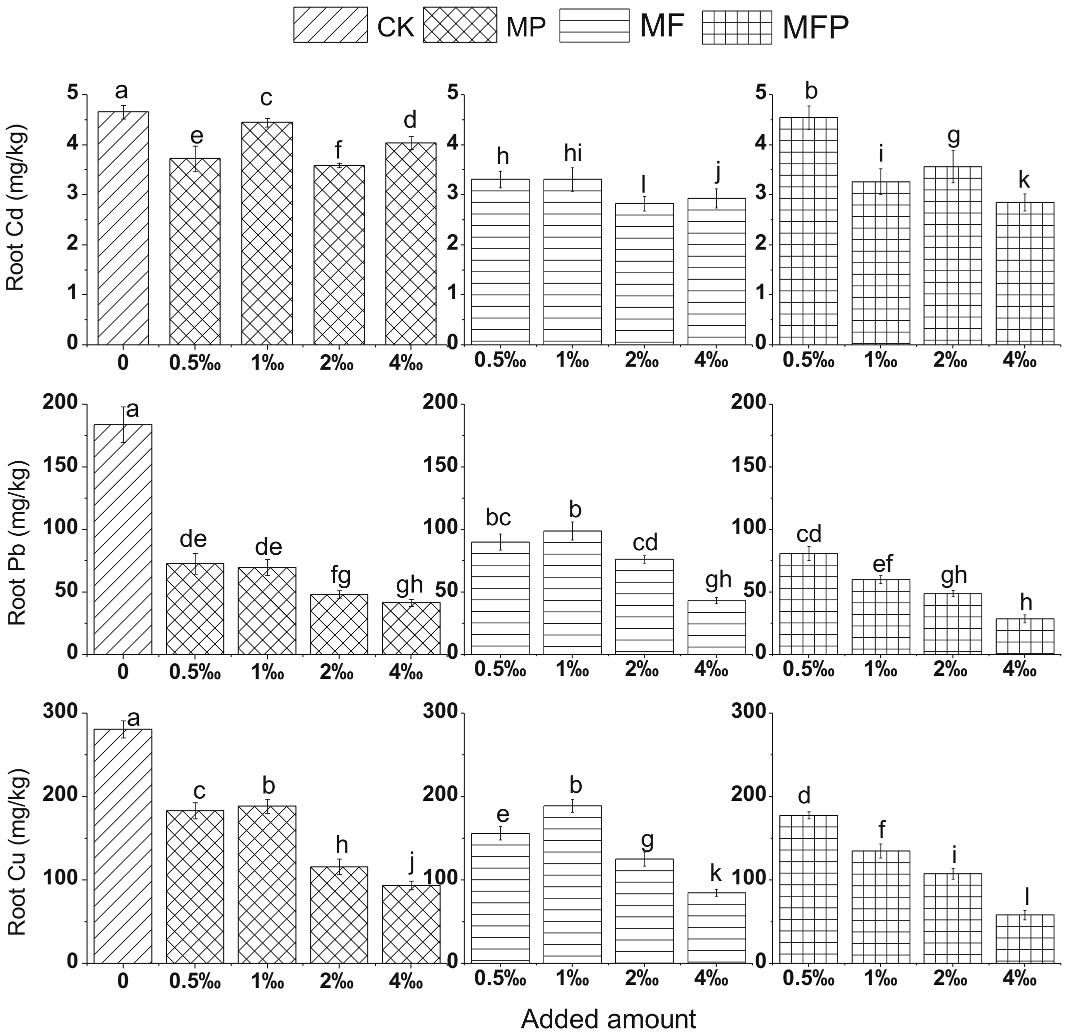

Fig. 6 Concentrations of Cd, Pb, and Cu in the root of pakchoi in different treatments (different letters identify the significant difference (P<0.05) among treatments)

significantly higher between shoot metal concentrations and extractable metal contents than between shoot metal concentrations and other parameters.

In addition to the reduction of bioavailable heavy metals in soil, the significant increase of available Ca (Table 3) can be related to the decrease of Cd uptake by plant. Specifically, it has been found that Ca as a plant nutrient can help to alleviate Cd toxicity where both Ca and Cd compete for the same Ca channels in plants (Nelson 1986; Tlustos et al. 2006). The application of MF and MFP was more effective in suppressing Cd uptake by the plants, probably due to its higher content of available silicon (Si), results that are similar to those reported by Chen et al. (2000).

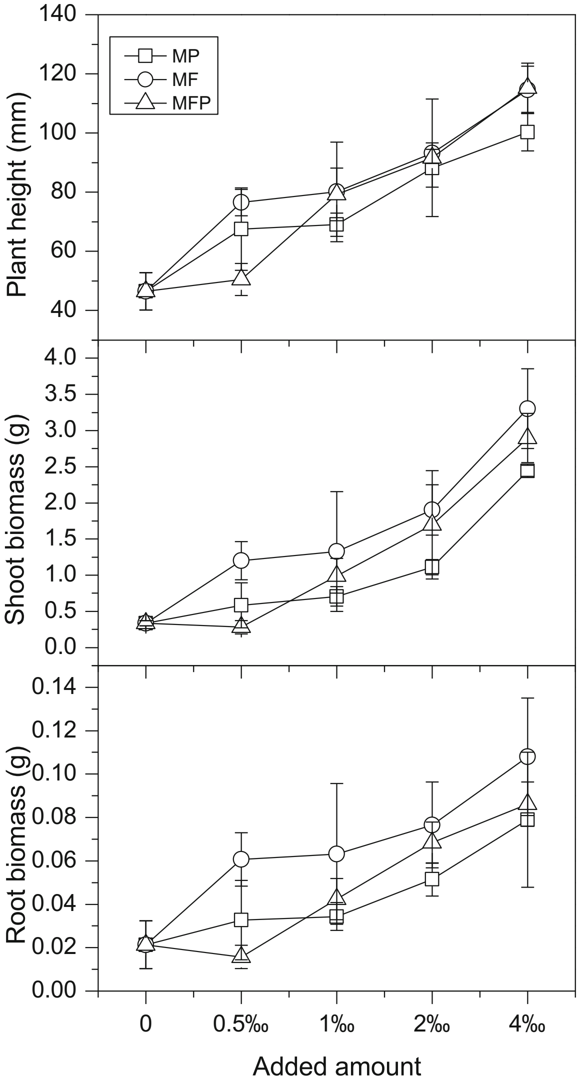

Fig. 7 The height and biomass of pakchoi in different treatments

Similar to the effect of Si on Cd uptake, Pb could be retained on the surface of the root due to binding to ion exchange sites and extracellular precipitation, mainly in the form of Pb phosphates especially in the MP treatment (Jarvis and Leung 2002).

3.5 Effect of the Amendments on Plant Growth

The effect of the amendments on the growth of pakchoi is shown in Fig. 7, which shows that almost all the amendments promoted the growth of pakchoi and increased its shoot biomass, root biomass, and height by 73.3–884 %, 53.2–406 %, and 8.64–146 %, respectively, relative to the control. Only in the 0.5‰ MFP treatment was there a slight decrease in shoot biomass and root biomass observed compared to the control.

Correlations were computed for the pakchoi growth vs various parameters in the soils amended with MP, MFP, and MFP (Table 5). A significantly positive correlation between the growth of pakchoi (biomass and height) and soil pH was observed for soils amended (Table 5). Therefore, the elevated pH was more suitable for the growth of pakchoi. This beneficial effect of soil pH neutralization on the biomass of pakchoi has also been observed in other studies (Zhou et al. 2005; He et al. 2009). The increased mineral nutrients (K, Ca, Mg, Si) also showed positive correlations with

Table 5 Correlation coefficients between soil properties studied and pakchoi growth index

	Shoot biomass	Root biomass	Plant height
pH	0.975**	0.940**	0.947**
Ava-K[a]	0.552	0.474	0.474
Ava-Ca	0.751**	0.606*	0.716**
Ava-Mg	0.880**	0.901**	0.860**
Ava-Si	0.930**	0.828**	0.865**
Ex-Cd[b]	−0.939**	−0.900**	−0.857**
Ex-Pb	−0.932**	−0.871**	−0.860**
Ex-Cu	−0.923**	−0.852**	−0.929**
Shoot Cd	−0.403	−0.515	−0.484
Shoot Pb	−0.757**	−0.724**	−0.830**
Shoot Cu	−0.830**	−0.833**	−0.906**
Root Cd	−0.770**	−0.684**	−0.773**
Root Pb	−0.613*	−0.575*	−0.910**
Root Cu	−0.818**	−0.786**	−0.910**

$^{*}P<0.05$, $^{**}P<0.01$

Ava available in soil, *Ex* exchangeable fraction of heavy meal in soil pakchoi growth (Table 5), especially the significantly elevated available Ca, Mg, and Si. Conversely, the significantly negative correlation between the growth of pakchoi (biomass and height) and the concentrations of heavy metals in the labile fraction (Table 5) suggests that these soil amendments can improve the growth of pakchoi by decreasing the availability of heavy metals in soil pools. Moreover, the correlation between heavy metals in pakchoi and the growth of pakchoi is significantly negative, indicating that the decrease of heavy metal uptake by the plant reduced the damage to pakchoi, a result similar to that observed by Chen and Zhang (Chen et al. 2011; Zhang et al. 2013). Overall, these results suggested that the increased pH, the elevated mineral nutrients, and the decreased toxicity of heavy metals associated with the soil amendments created much more suitable soil conditions for pakchoi growth.

4 Conclusion

This study evaluated the application of three modified industrial by-products as soil amendments in the restoration of heavy metal-contaminated agricultural lands. Cd, Pb, and Cu immobilization, soil quality improvement, and pakchoi growth response were evaluated when these soil amendments were applied at four application rates. The most effective mixture for all the amendments was 4‰ *w/w*.

The application of the three modified industrial by-products was effective in immobilizing Cd, Cu, and Pb in soil and reducing their bioavailability to pakchoi. The significant conversion of heavy metal fractions (from labile fractions to stable fractions) was mainly attributed to the increased soil pH and the function of elevated Ca, Si, and P contents. MF and MFP were more effective in the immobilization of Cd, mainly due to elevated levels of available Si in soil; the P-rich amendment (MP) was more effective for Pb retention; and all three types of amendments were effective in decreasing the availability of Cu.

In addition to the immobilization of heavy metals, the amendments improved soil quality. The addition of the three alkaline amendments neutralized the acidity of the soil and increased soil pH by 0.13–1.26 units. Since all of the amendments are rich in available Ca, Mg, and Si, especially MF and MFP, the addition of the amendments increased soil Ca, Mg, and Si content as a whole. The application of P-rich amendment (MP) enhanced soil available P significantly ($p<0.05$), and the increase of available K reached statistical significance in MF and MFP treatments.

All the amendments promoted the growth of pakchoi and increased the shoot biomass, root biomass, and height of pakchoi. The increased pH, the elevated mineral nutrients, and the decreased toxicity of heavy metals created a much more suitable soil condition for pakchoi growth due to the amendments addition.

We conclude that the application of the three modified industrial by-products as soil amendments had a demonstrably positive impact on the remediation and revitalization of heavy metal-contaminated agricultural soil. However, further studies are needed in order to investigate the effects of the amendments on the biological environment of heavy metal-contaminated soil.

Acknowledgments All the authors gratefully acknowledge the financial support of National Natural Sciences Foundation of China (Project U1301231), Natural Sciences Foundation of Guangdong Province (Project S2011020005187), and Science and Technology Support Plan of Guangzhou (Projects 11A92081308).

References

Acquaye, D., & Tinsley, J. (1965). *Soluble silica in soils*. London: Proceedings of the Eleventh Easter School in Agricultural Science, University of Nottingham, 1964, Butterworths.

Adriano, D., Wenzel, W., Vangronsveld, J., & Bolan, N. S. (2004). Role of assisted natural remediation in environmental cleanup. *Geoderma, 122*(2), 121–142.

Ahmad, M., Hashimoto, Y., Moon, D. H., Lee, S. S., & Ok, Y. S. (2012). Immobilization of lead in a Korean military shooting range soil using eggshell waste: an integrated mechanistic approach. *Journal of Hazardous Materials, 209*, 392–401. doi:10.1016/j.jhazmat.2012.01.047.

Appel, C., & Ma, L. (2002). Concentration, pH, and surface charge effects on cadmium and lead sorption in three tropical soils. *Journal of Environmental Quality, 31*(2), 581–589.

Badreddine, R., Humez, A. N., Mingelgrin, U., Benchara, A., Meducin, F., & Prost, R. (2004). Retention of trace metals by solidified/stabilized wastes: assessment of long-term metal release. *Environmental Science & Technology, 38*(5), 1383–1398. doi:10.1021/es0209520.

Bolan, N. S., Adriano, D. C., Duraisamy, P., Mani, A., & Arulmozhiselvan, K. (2003). Immobilization and phytoavailability of cadmium in variable charge soils. I. Effect of phosphate addition. *Plant and Soil, 250*(1), 83–94. doi:10.1023/a:1022826014841.

Cao, X. D., Ma, L. Q., Chen, M., Singh, S. P., & Harris, W. G. (2002). Impacts of phosphate amendments on lead biogeochemistry at a contaminated site. *Environmental Science & Technology, 36*(24), 5296–5304. doi:10.1021/es020697j.

Cao, X., Dermatas, D., Xu, X., & Shen, G. (2008). Immobilization of lead in shooting range soils by means of cement, quicklime, and phosphate amendments. *Environmental Science* *and Pollution Research, 15*(2), 120–127. doi:10.1065/espr2007.05.416.

Chen, X. B., Wright, J. V., Conca, J. L., & Peurrung, L. M. (1997). Evaluation of heavy metal remediation using mineral apatite. *Water, Air, and Soil Pollution, 98*(1–2), 57–78. doi:10.1007/bf02128650.

Chen, H. M., Zheng, C. R., Tu, C., & Shen, Z. G. (2000). Chemical methods and phytoremediation of soil contaminated with heavy metals. *Chemosphere, 41*(1–2), 229–234. doi:10.1016/s0045-6535(99)00415-4.

Chen, X., Wang, J., Shi, Y., Zhao, M. Q., & Chi, G. Y. (2011). Effects of cadmium on growth and photosynthetic activities in pakchoi and mustard. *Botanical Studies, 52*(1), 41–46.

EPA. (1986). *Test methods for evaluating solidwaste, Laboratory Manual Physical/Chemical Methods. (Vol. SW-846)*. Washington, DC: U.S. Government Printing Office.

Friesl, W., Horak, O., & Wenzel, W. W. (2004). Immobilization of heavy metals in soils by the application of bauxite residues: pot experiments under field conditions. *Journal of Plant Nutrition and Soil Science-Zeitschrift Fur Pflanzenernahrung Und Bodenkunde, 167*(1), 54–59. doi:10.1002/jpln.200320941.

Garrido, F., Illera, V., & Garcia-Gonzalez, M. T. (2005). Effect of the addition of gypsum- and lime-rich industrial by-products on Cd, Cu and Pb availability and leachability in metal-spiked acid soils. *Applied Geochemistry, 20*(2), 397–408. doi:10.1016/j.apgeochem.2004.08.001.

He, M. M., Li, W. H., Liang, X. Q., Wu, D. L., & Tian, G. M. (2009). Effect of composting process on phytotoxicity and speciation of copper, zinc and lead in sewage sludge and swine manure. *Waste management (New York, N.Y.), 29*(2), 590–597. doi:10.1016/j.wasman.2008.07.005.

Hong, C. O., Lee, D. K., Chung, D. Y., & Kim, P. J. (2007). Liming effects on cadmium stabilization in upland soil affected by gold mining activity. *Archives of Environmental Contamination and Toxicology, 52*(4), 496–502. doi:10.1007/s00244-006-0097-0.

Janoš, P., Vávrová, J., Herzogová, L., & Pilařová, V. (2010). Effects of inorganic and organic amendments on the mobility (leachability) of heavy metals in contaminated soil: a sequential extraction study. *Geoderma, 159*(3), 335–341.

Jarvis, M. D., & Leung, D. W. M. (2002). Chelated lead transport in Pinus radiata: an ultrastructural study. *Environmental and Experimental Botany, 48*(1), 21–32. doi:10.1016/s0098-8472(02)00005-9.

Kumpiene, J., Lagerkvist, A., & Maurice, C. (2008). Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments—a review. *Waste Management, 28*(1), 215–225. doi:10.1016/j.wasman.2006.12.012.

Lee, S.-H., Kim, E. Y., Park, H., Yun, J., & Kim, J.-G. (2011a). In situ stabilization of arsenic and metal-contaminated agricultural soil using industrial by-products. *Geoderma, 161*(1–2), 1–7. doi:10.1016/j.geoderma.2010.11.008.

Lee, S.-H., Park, H., Koo, N., Hyun, S., & Hwang, A. (2011b). Evaluation of the effectiveness of various amendments on trace metals stabilization by chemical and biological methods. *Journal of Hazardous Materials, 188*(1–3), 44–51. doi:10.1016/j.jhazmat.2011.01.046.

Ma, Q. Y., Logan, T. J., & Traina, S. J. (1995). Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. *Environmental Science & Technology, 29*(4), 1118–1126.

Matusik, J., Bajda, T., & Manecki, M. (2008). Immobilization of aqueous cadmium by addition of phosphates. *Journal of Hazardous Materials, 152*(3), 1332–1339. doi:10.1016/j.jhazmat.2007.08.010.

McGowen, S. L., Basta, N. T., & Brown, G. O. (2001). Use of diammonium phosphate to reduce heavy metal solubility and transport in smelter-contaminated soil. *Journal of Environmental Quality, 30*(2), 493–500.

Mench, M., Vangronsveld, J., Clijsters, H., Lepp, N. W., & Edwards, R. (2000). *In situ metal immobilisation and phytostabilization of contaminated soils (phytoremediation of contaminated soil and water)*. Boca Raton, FL: Lewis Publishers.

MEPC (2014). The Bulletin of Soil Pollution Situation Investigation of PR China. In M. o. E. P. o. China, & M. o. L. a. Resources (Eds.), (pp. 5).

Mulligan, C. N., Yong, R. N., & Gibbs, B. F. (2001). Remediation technologies for metal-contaminated soils and groundwater: an evaluation. *Engineering Geology, 60*(1–4), 193–207. doi:10.1016/s0013-7952(00)00101-0.

Narwal, R. P., Singh, B. R., & Salbu, B. (1999). Association of cadmium, zinc, copper, and nickel with components in naturally heavy metal-rich soils studied by parallel and sequential extractions. *Communications in Soil Science and Plant Analysis, 30*(7–8), 1209–1230. doi:10.1080/00103629909370279.

Nelson, M. T. (1986). Interactions of divalent cations with single calcium channels from rat brain synaptosomes. *The Journal of General Physiology, 87*(2), 201–222. doi:10.1085/jgp.87.2.201.

Nelson, D. W., & Sommers, L. E. (1982). Total carbon, organic carbon, and organic matter. In D. R. Keeney (Ed.), *Methods of soil analysis, part 2: chemical and microbio-logical properties* (Vol. 9, pp. 539–577). Madison, WI: ASA.

Noble, A. D., & Hurney, A. P. (2000). Long-term effects of lime additions on sugarcane yield and soil chemical properties in north Queensland. [Article]. *Experimental Agriculture, 36*(3), 397–413. doi:10.1017/s0014479700003112.

Ok, Y. S., Chang, S. X., & Feng, Y. S. (2007). Sensitivity to acidification of forest soils in two watersheds with contrasting hydrological regimes in the oil sands region of Alberta. *Pedosphere, 17*(6), 747–757. doi:10.1016/s1002-0160(07)60090-3.

Ok, Y. S., Lim, J. E., & Moon, D. H. (2011). Stabilization of Pb and Cd contaminated soils and soil quality improvements using waste oyster shells. *Environmental Geochemistry and Health, 33*(1), 83–91. doi:10.1007/s10653-010-9329-3.

Padmavathiamma, P. K., & Li, L. Y. (2010). Phytoavailability and fractionation of lead and manganese in a contaminated soil after application of three amendments. *Bioresource Technology, 101*(14), 5667–5676. doi:10.1016/j.biortech.2010.01.149.

Sarwar, N., Saifullah, T., Malhi, S. S., Zia, M. H., Naeem, A., Bibi, S., et al. (2010). Role of mineral nutrition in minimizing cadmium accumulation by plants. *Journal of the Science of Food and Agriculture, 90*(6), 925–937. doi:10.1002/jsfa.3916.

Shashkova, I. L., Rat'ko, A. I., & Kitikova, N. V. (1999). Removal of heavy metal ions from aqueous solutions by alkaline-earth metal phosphates. *Colloids and Surfaces a-Physicochemical and Engineering Aspects, 160*(3), 207–215. doi:10.1016/s0927-7757(99)00193-4.

Shi, L., Xu, P., Xie, K., Tang, S., & Li, Y. (2011). Preparation of a modified flue gas desulphurization residue and its effect on pot sorghum growth and acidic soil amelioration. *Journal of Hazardous Materials, 192*(3), 978–985. doi:10.1016/j.jhazmat.2011.05.102.

Stehouwer, R., Sutton, P., Fowler, R., & Dick, W. (1995). Minespoil amendment with dry flue gas desulfurization by-products: element solubility and mobility. *Journal of Environmental Quality, 24*(1), 165–174.

Tencent (2012). Heavy metals in soil polluted million tons of grain per year and fish were poisoned to death in heavy metal polluted surface water. http://news.qq.com/a/20120613/000024_1.htm.

Tessier, A., Campbell, P. G., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry, 51*(7), 844–851.

Tlustos, P., Szakova, J., Korinek, K., Pavlikova, D., Hanc, A., & Balik, J. (2006). The effect of liming on cadmium, lead, and zinc uptake reduction by spring wheat grown in contaminated soil. *Plant, Soil and Environment, 52*(1), 16–24.

Vieira da Cunha, K. P., & Araujo do Nascimento, C. W. (2009). Silicon effects on metal tolerance and structural changes in Maize (Zea mays L.) grown on a cadmium and zinc enriched soil. *Water, Air, and Soil Pollution, 197*(1–4), 323–330. doi:10.1007/s11270-008-9814-9.

Watanabe, F., & Olsen, S. (1965). Test of an ascorbic acid method for determining phosphorus in water and NaHCO3 extracts from soil. *Soil Science Society of America Journal, 29*(6), 677–678.

Zhang, D.-g., Liu, Y.-h., Yang, R.-p., & He, F.-f. (2013). Influence of compound heavy metal pollution on three kinds of vegetables growth status and physiological and biochemical characteristics. In X. Tang, W. Zhong, D. Zhuang, C. Li, & Y. Liu (Eds.), *Progress in Environmental Protection and Processing of Resource, Pts 1–4* (Vol. 295–298, pp. 100–103, Applied Mechanics and Materials).

Zhou, D. M., Hao, X. Z., Wang, Y. J., Dong, Y. H., & Cang, L. (2005). Copper and Zn uptake by radish and pakchoi as affected by application of livestock and poultry manures. *Chemosphere, 59*(2), 167–175. doi:10.1016/j.chemosphere.2004.11.008.