Effects of Soil Amendments on the Extractability and Speciation of Cadmium, Lead, and Copper in a Contaminated Soil

Dasong Lin · Qixing Zhou

Abstract The effects of chemical amendments including zeolite, compost and mesoporous molecular sieves (MCM-41) on the extractability and speciation of heavy metals (Cd, Pb and Cu) in a contaminated soil were investigated. Results showed that the application of soil amendments decreased Cd, Pb and Cu uptake by the shoots of pakchoi, up to 44.2–53.2%, 30.2–42.7% and 16.9–22.1%, respectively, compared with the control. Among the three amendments, zeolite and MCM-41 were more efficient in reducing Cd and Cu uptake, while compost was more efficient in reducing Pb uptake by the plants. The growth of pakchoi was improved in amended soils due to the action of chemical amendments.

Keywords Soil · Heavy metal · Amendment · Bioavailability · Chemical extractability

Soils contaminated with heavy metals may cause long-term risks threatening entire ecosystems and human health. The risk associated with such sites depends on soil characteristics (e.g. content of clay, sesquioxides, organic matter, and pH), climate factors (e.g. precipitation, winds and temperature), and environmental behaviors of the toxic contaminants (Filius et al. 1998; Zhou 2003). The application of soil amendments to immobilize heavy metals is a promising technology to meet the requirements for environmentally sound and cost-effective remediation (Gupta et al. 2007). In particular, chemical immobilization is a promising technique to reduce the mobility of toxic contaminants in the ecosystems; it involves the addition of chemical and mineralogical materials to the contaminated soils to reduce the solubility and bioavailability of toxic metals through sorption and/or precipitation. The objectives of the present work were (1) to examine the effects of compost, zeolite and the mesoporous molecular sieves (MCM-41) on the mobility of heavy metals in polluted soil; (2) to evaluate the effectiveness of various chemical treatments on the uptake of Cd, Pb and Cu by vegetables such as pakchoi (*Brassica chinensis*) in greenhouse conditions; (3) to investigate the changes in the speciation of Cd, Pb and Cu after application of different chemical treatments using sequential fractionation methods.

Materials and Methods

The surface (<20 cm) soil samples used for this study was collected from various contaminated sites of a typical polluted field in Zhejiang Province, China. This soil was co-contaminated with Cd, Pb and Cu, due to local nonferrous metallurgical industry. After transportation to the laboratory, the soil was air-dried and sieved (<2 mm) prior to use. Chemical characteristics of the soil and its metal concentrations were listed in Tables 1 and 2, where soil pH (soil: water = 1:1) was measured by the combination electrode, organic carbon was determined by the Walkley–Black wet combustion method, and total metal contamination in the soil was analyzed using the atomic absorption spectroscopy with the flame or flameless mode following $HF–HNO_3–HClO_4$ digestion procedures (Lu 1999). In addition, particle size analysis using the hydrometer

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Table 1 Changes in chemical characteristics of the tested soil after amending

	Control-soil	Zeolite-soil	Compost-soil	MCM-41-soil
pH (in H_2O)	5.8	6.1	6.9	6.4
Total organic C (g kg^{-1})	32.4	32.0	45.3	32.2
Total nitrogen (g kg^{-1})	2.3	2.1	3.7	2.0
Available P (g kg^{-1})	4.8	4.5	94.7	4.5

Table 2 Total and extractable metals in soil (mg kg^{-1})

Treatment	Total	NH$_4$OAc	HOAc	EDTA	DTPA
Cd					
Control	5.27[a]	1.67[a]	3.77[a]	4.01[a]	4.28[a]
Zeolite	5.23[a]	1.51[b]	2.91[c]	3.75[b]	3.89[c]
Compost	5.26[a]	1.62[a]	3.15[b]	3.86[b]	3.92[b]
MCM-41	5.25[a]	1.55[b]	2.83[c]	3.52[c]	3.66[c]
Pb					
Control	633[a]	14.8[a]	37.8[a]	339[a]	432[a]
Zeolite	629[a]	13.1[c]	32.2[b]	306[d]	405[b]
Compost	634[a]	14.2[b]	25.7[d]	316[b]	372[d]
MCM-41	633[a]	12.9[d]	31.3[c]	309[c]	401[c]
Cu					
Control	257[a]	5.67[a]	32.5[a]	197[a]	159[a]
Zeolite	255[a]	4.71[c]	27.9[c]	181[d]	149[c]
Compost	259[a]	4.98[d]	29.1[b]	189[b]	154[b]
MCM-41	255[a]	4.69[c]	27.4[c]	183[c]	148[c]

Data with the same letter within the same column do not differ significantly at the 5% level according to least significant difference test

method (Lu 1999) indicated the soil was a sandy loam (the USDA classification) with 51% sand, 29% silt, and 20% clay.

After the natural zeolite used in the experiment was collected from a layer found in Jinyun County, Zhejiang Province, China, it was finely ground, sieved through <0.02 mm and washed with distilled water prior to the measurement of the sorption capacity. The mineralogical composition of the zeolite was clinoptilolite (65%wt), quartz (18%wt), feldspar (5%wt), opal (6%wt), smectite (3%wt), ematite (1%wt) and mica (2%wt). The pH value, determined in a 1:2.5 ratio of zeolite/distilled water, was 7.8. The cation exchange capacity (CEC) determined with BaCl$_2$–triethanolamine following the usual international methods (Lu 1999) was 190 cmol (+)/kg. The compost used in this study was obtained by having mixed two proportions (v/v) of pig manure (70%) and vegetal waste (30%). The total organic carbon was 279.2 g kg^{-1} dry weight (DW), total nitrogen was 20.6 g kg^{-1} DW, and total Cd, Pb and Cu concentrations were 1.04, 14.3 and 37.7 mg kg^{-1} DW, respectively. MCM-41 was synthesized with hexadecyl trimethyl ammonium bromide (CTMA-Br), tetramethyl ammonium hydroxide (TMA-OH), tetraethyl

orthosilicate (TEOS), and H$_2$O (Lin and Xu 2006). Its specific surface area (SE) determined with the single point BET N$_2$ adsorption method was 865 m^2 g^{-1}. Its total number of sites available (Ns) determined with acid–base titration was 8.24 -OH/A$_2$.

Different chemical treatments were used to compare and evaluate the effectiveness of chemical remediation techniques. Soil samples (1.0 kg) were put to polyethylene (25 cm in diameter and 35 cm in height) pots, after they were treated by one of the following methods: (1) 1% zeolite (10 g); (2) 2% compost (20 g); (3) 0.5% MCM-41 (5 g); and (4) the unamended control. There were four replicates for each treatment. Soil amendments were thoroughly mixed with soil samples which were supplemented with nitrogen (0.2 g N kg^{-1} soil as NH$_4$NO$_3$) and potassium (0.125 g K kg^{-1} soil as KCl) fertilizers. Deionized water was added in order to sustain 20% of the soil water-holding capacity. The pots were placed in an incubator at room temperature (25°C) and 70% of the relative humidity. After a 4-week incubation period, ten pakchoi seeds were sown in each pot. The young seedlings were thinned to five per pot, 7 days after the seed germination. During the experiment, water in pots was made up with deionized water according to water loss by weighing it. The pots were placed in a random complete block design (RCBD) under glasshouse conditions (temperature = 15–25°C, and relative humidity = 60–70%). Plants were harvested 2 months after the seed germination.

After having harvested, plant roots were carefully removed from each pot and washed thoroughly to get rid of adhering soil particles followed by quick wash in deionized water. Soil samples in each pot were kept for further analysis. Then roots and shoots were oven-dried at 60°C for 72 h, and their dry weights were recorded. The growth of the vegetable in each treatment was evaluated by measuring several parameters (length of shoots and roots, and their wet and dry weights).

The concentration of heavy metals including Cd, Pb and Cu in the soil was measured after digestion with HNO$_3$ and HCl (1:3 v/v) using a microwave digester (MLS 1200). The concentration of the heavy metals in the roots and shoots of the vegetable was analyzed by digesting them in 2N HNO$_3$ solution after having incinerated the plant samples in a muffle furnace at 650°C (Martin-Prevel et al. 1987). The digested solutions were filtered and diluted to 25 mL in

volumetric flasks and stored at 4°C prior to the analysis using a flame atomic absorption spectrophotometer (Thermo Elemental SOLAAR-M6). The concentrations of heavy metals are expressed as a fraction of plant dry matter. Metals extracted by 1 M NH₄OAc (pH 7.0) (Mench et al. 1994), 0.43 M HOAc (Mench et al. 1994), 0.05 M EDTA (pH 7.0; Norvell 1984), and DTPA–TEA (0.005 M diethylenetriaminepentaacetic acid, 0.1 M triethanolamine, and 0.01 M CaCl₂ at pH 7.3 (Lindsay and Norvell 1978; Zhou et al. 2001; Zhou and Sun 2002). The extraction solutions were filtered with a Whatman filter paper No. 42. The concentrations of Cd, Pb and Cu in the filtrate were also determined by a flame atomic absorption spectrophotometer (Thermo Elemental SOLAAR-M6). Sequential extraction of Cd, Pb and Cu in soil samples from each pot after having air-dried (1.0 g in 50-mL polyethylene centrifuge tubes) was performed according to Mench et al. (1994) and Zhou et al. (2001).

Results and Discussion

Soil pH was affected to a certain extent by the application of various amendments. The application of compost increased soil pH from 5.8 to 6.9 (Table 1). However, there were a few effects on soil pH by the application of zeolite or MCM-41. The increase in soil pH is responsible for the dissolution of amendments. Immobilization of heavy metals through the process of ion exchanges and surface complexation can be promoted when soil pH increases. The addition of compost also resulted in an increase in available phosphorus, organic carbon and total nitrogen (Table 1).

Total Cd, Pb and Cu in the tested soil were high, up to 5.27, 633 and 257 mg kg⁻¹, respectively. The application of amendments did not statistically modify the total concentrations of Cd, Pb and Cu in soil. However, it was indicated that there were a significant decrease (Table 2) in the extractability of soil Cd, Pb and Cu by HOAc, EDTA and DTPA. The differences between NH₄OAc and extractable Cd in soil were small when the differences between NH₄OAc and extractable Pb or Cu became great. In particular, quadratic contrasts for NH₄OAc-extractable Pb and Cu were significant (Both $p < 0.05$). By and large, the sequence in the amount of metals extracted by the four extractants was DTPA > EDTA > HOAc > NH₄OAc for Cd and Pb, and EDTA > DTPA > HOAc > NH₄OAc for Cu (Table 2).

Although there has been much debate about which part of metals in soils is the 'bioavailable' fraction, plant uptake in amended soils has often been correlated with some extractable fraction of metals in soils. A wide range of extractants including EDTA, DTPA, NH₄NO₃ and HOAc have been applied with varying success, but there is no
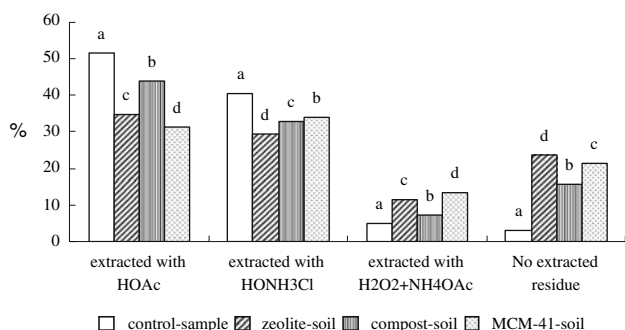
fully satisfactory extractant for all soil–plant systems because of varying properties of different soils and plant species. Considerable efforts have been made to accurately measure extractable metal concentrations in soil samples (Quevauviller 1998). In this study, metal extractability was greatly different using the four extractants. NH₄OAc is a mild extractant that can extract only the easily exchangeable metals, HOAc can dissolve part of the metals from soil solids because of its weak acidity, and EDTA is the strongest extractant among the four extractants. The EDTA-extractable metals were considered to be associated with the specifically adsorbed metals. Generally speaking, DTPA is most suitable for calcareous soils, as it is buffered at pH 7.3 and therefore prevents CaCO₃ from dissolution and release of occluded metals (Lindsay and Norvell 1978). The DTPA extractant contains (1) a high concentration of CaCl₂, of which Ca may exchange rapidly with bivalent cations, especially Cd and Pb in the case of the acidic soil, (2) a high chloride concentration, which complexes these two elements, and (3) triethanolamine (TEA), which is protonated at pH 7.3 and could exchange H⁺ with cations from the exchange sites as suggested by Lindsay and Norvell (1978). The results obtained from these extraction studies give a measure of metal potential mobility as an approximation to the potential risk of metal pollution in natural waters or plants, allowing to determine the suitability or unsuitability of the soil treatments.

The recovery of metals using the sequential extraction procedure (SEP) was calculated by comparing the sum of the four fractions against the total metal concentration measured. The recovery ranged between 95% for Cd and 112% for Pb. SEP used to investigate the distribution of metals in the control soil showed that Cd has a distribution pattern with the 'HOAc-soluble' and 'reducible' fractions accounted for containing the most part of the metal. The addition of soil amendments, particularly MCM-41, significantly reduced exchangeable Cd. On the contrary, the fraction of metals associated with organically bound and sulfide fraction ('oxidisable' fraction) increased in all amended soil samples. Particularly in the MCM-41 treatment, the oxidisable fraction of Cd increased greatly, up to 2.6 times as much as that in the control. Also in the amended soil samples, all the amendments caused an increase in the non-extracted form (residue) of Cd compared with that in the control, up to 8.4 times for zeolite, 5.0 times for compost and 6.8 times for MCM-41, respectively (Fig. 1). In the control soil samples, Pb was associated with the HOAc-soluble (16%) (weakly bound with organic matter and carbonates), iron and manganese oxides (36%), organically bound and sulfide (35%) fractions. The application of soil amendments changed the distribution of Pb forms from the exchangeable fraction to the 'reducible' and 'oxidisable' fractions. Application of
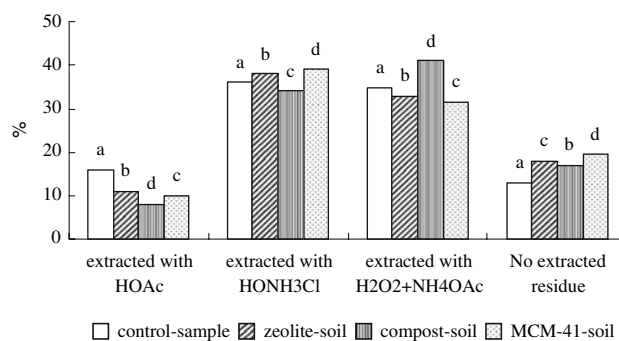
soil amendments significantly increased the residual fraction of Pb in soil, the residual fraction increased in comparison with the control by up to 1.4 times for zeolite, 1.3 times for compost and 1.5 times for MCM-41 as much as that in the control, respectively (Fig. 2). However, Mench et al. (1994) showed a reduction in exchangeable Pb and Cd due to the application of various soil amendments using the similar SEP method. As expected, Cu was associated primarily with organically bound and sulfide fraction (51%) and the amendments used in this study were efficient in significantly reducing the exchangeable Cu fraction. On the contrary, the addition of amendments led to a dramatic increase in reducible Cu and the residual fraction (Fig. 3).

Various amendment materials such as lime, compost, zeolite, hydroxyapatite, phytate have been widely used to immobilize metals in soils to reduce its phytotoxicity and accumulation by plants (Berti and Cunningham 1997; Cao et al. 2003; Basta and Gradwohl 2000; Chen et al. 2000). The formation of zeolite or other compounds with low solubility and the transformation of metal forms from the exchangeable (or available) fractions to unavailable fractions are key processes of metal immobilization (Cao et al. 2003). In general, there was an increased residual fraction of heavy metals by the action of soil amendments, probably due to the formation of strong bonds between the metals and the adsorbing surface of the zeolite-soil, compost-soil and MCM-41-soil.

Table 3 shows the concentrations of the three metals in the roots and shoots (leaves plus stems) of pakchoi plants grown in the soil samples. The chemical amendments applied were very efficient in reducing metal uptake by the plants. Among the three amendments, zeilite and MCM-41 were more efficient in reducing Cd and Cu uptake by the plants. The concentration of Cd in the shoots of plants grown in zeolite-soil and MCM-41-soil was 53.2 and 51.1% lower than that in the control, respectively. The zeolite and MCM-41 treatments decreased the concentration of Cu in the shoots of plants by 24.6 and 23.8%,

Fig. 2 Pb fractions extracted from soil samples (Values followed by the same letter within the same group do not differ significantly at the 5% level according to the least significant difference test)
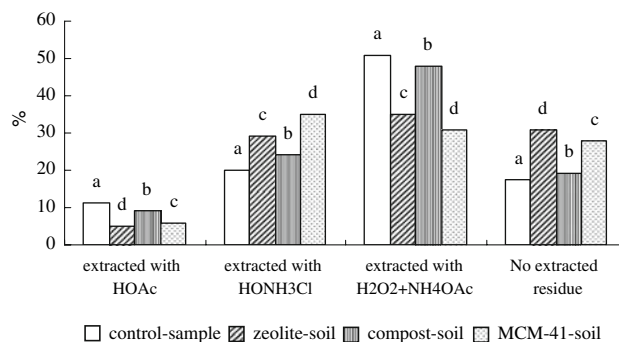
Fig. 3 Cu fractions extracted from soil samples (Values followed by the same letter within the same group do not differ significantly at the 5% level according to the least significant difference test)

respectively (Table 3). Compost was more efficient in reducing Pb uptake by plants. The concentration of Pb in the roots and shoots of plants grown in compost-soil was 23.4 and 42.7% lower than that in the control, respectively. It seems clear that the decreased uptake of metals by the plants grown in the amended soils was related to the increase of soil pH and the fixation of available metals in soils (Chen et al. 2000; Lombi et al. 2002).

Generally speaking, the amount of Cd, Pb and Cu taken up by the plants accumulated mainly in the roots, and this is in agreement with results from other researchers (Lombi

Fig. 1 Cd fractions extracted from soil samples (Values followed by the same letter within the same group do not differ significantly at the 5% level according to the least significant difference test)

Table 3 Changes in the concentrations of Cd, Pb and Cu in pakchoi plants due to application of amendments (mg kg^{-1})

Treatment	Cd		Pb		Cu	
	Root	Shoot	Root	Shoot	Root	Shoot
Control	4.13[a]	1.90[a]	12.5[a]	0. 96[a]	10.2[a]	6.15[a]
Zeolite	1.78[d]	0.89[c]	10.8[b]	0.67[c]	7.61[d]	4.79[c]
Compost	2.16[b]	1.06[b]	9.58[c]	0.55[d]	8.57[b]	5.11[b]
MCM-41	1.98[c]	0.93[c]	10.7[b]	0.61[c]	8.18[c]	4.84[c]

Data with the same letter within the same column do not differ significantly at the 5% level according to least significant difference test

Table 4 Changes in the growing length and biomass (mean) of the pakchoi plants due to application of amendments

Treatment	Shoot length (cm)	Root length (cm)	Shoot biomass (g)	Root biomass (g)
Control	15.0[a]	5.71[a]	1.77[a]	0.24[a]
Zeolite	16.1[a]	6.44[a]	2.13[b]	0.41[b]
Compost	17.3[b]	6.92[b]	2.87[c]	0.55[c]
MCM-41	16.6[a]	6.84[b]	2.35[b]	0.49[b]

Data with the same letter within the same column do not differ significantly at the 5% level according to least significant difference test

et al. 2002; Zornoza et al. 2002). The translocation of Pb from roots to shoots was lower for the vegetable grown in the control (shoot Pb: root Pb = 0.08). By contrast, less Cd was retained in the root systems. Although the plants grown in the amended soils taken up the lowest quantity of this metal, they had the highest shoot: root ratio (0.50 for zeolite-soil, 0.49 for compost-soil and 0.47 for MCM-41-soil, respectively). Whereas Cu translocation was the same in the vegetable grown in all the soils (shoot Cu: root Cu = 0.6).

Table 4 shows that the application of chemical amendments increased the shoot and root biomass because they increased soil pH and improved the growing conditions for the plants. The lower shoot and root biomass in the control may be related to the low soil pH and a low tolerance of pakchoi to acid conditions as well as to the toxicity of metals in the control soil containing high Cd, Pb and Cu concentration. Chemical amendments had beneficial effects on the growth of plants because all treatments with amendments had a higher biomass or yield compared with the control. In other words, the shoot biomass increased 1.2 times for the soil amended with zeolite, 1.6 times for the soil amended with compost, and 1.3 times for the soil amended with MCM-41 as much as that in the control, and root also increased 1.7 times for the soil amended with zeolite, 2.3 times for the soil amended with compost, and 2.0 times for the soil amended with MCM-41 as much as that in the control. According to Chen et al. (2000), the application of chemical amendments alleviated the phytotoxicity of heavy metals and had beneficial effects on plant growth.

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