Effect of bone char application on Pb bioavailability in a Pb-contaminated soil

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Bone char amendments show potential for remediation of Pb-contaminated soils.

Abstract

The effects of bone char (BC) application on the bioavailability of Pb in a polluted soil from Hunan Province, China were examined. The Pb-contaminated soil was treated with two types of bone char, one from the UK and the other from China. The bioavailability of Pb was determined in terms of the uptake by Chinese cabbage (*Brassica chinensis* L.), sequential extraction and X-ray diffraction analysis. The results indicate that the Pb concentrations in both shoots and roots decreased with increasing quantities of added bone char, and the application of BC from the UK at the rate of 1.6% (w:w) had the largest effect. Lead Pb concentrations in the shoots and roots decreased by 56.0% and 75.9%, respectively, whereas the application of BC from Zhejiang Province, China at the rate of 1.6% (w:w) reduced Pb concentrations in the shoots and roots to 2.04 mg kg⁻¹ and 8.42 mg kg⁻¹, respectively, only 45.8% and 30.2% compared to the control treatment. Sequential extraction results indicate that the addition of bone char, as a metal-immobilizing agent, substantially transforms soil Pb from non-residual fractions to the residual fraction. The transformation was further confirmed using X-ray diffraction studies.

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1. Introduction

Accumulation of heavy metals in soils and their transport through the food chains are potential threats to human health, especially to children's health by ingestion of Pb-contaminated soil (Melamed et al., 2003). Although some sources of Pb contamination have been reduced worldwide (e.g., from Pb alkyls in gasoline), Pb emission to the environment is still increasing in many

countries (Adriano, 2001). It has been estimated that the Pb loading rate to soil exceeds its natural removal rate by approximately 20-fold or more (Nriagu, 1988). Most soil contamination is due to anthropogenic sources, such as mining and smelting, combustion of leaded gasoline, land application of sewage sludge, battery disposal and lead pellets (Adriano, 2001). Increasing awareness of the hazards that toxic elements can cause to the environment and to humans makes it necessary to remediate metal-contaminated sites.

Changsha city, the capital of Hunan Province, China is a modern industrial city surrounded by agricultural areas. The major types of industry are machinery, metallurgy, chemical and production of building materials.

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Investigation and assessment of pollution sources showed that the key pollution sources are from industrial waste gas and wastewater. Industrial activities there have resulted in significant heavy metal pollution on a large scale, with the consequence that elevated heavy metal concentrations in water, soil and locally grown vegetables and crops may greatly exceed accepted standards and thus pose a severe threat to human health.

Three different strategies can be adopted for the restoration of highly metal-contaminated sites (Zwonitzer et al., 2003). The most clear-cut solution is to remove the polluted substrates and to replace with unpolluted soil. On a large scale, however, this type of solution is not feasible due to high costs. A second possible remediation approach is soil cleaning by means of chemical, physico-chemical or biological techniques, which remove the metals from the soil. However, these techniques may create new problems, such as increased metal mobility and bioavailability, redistribution of the pollutants to sludge and changes in physico-chemical characteristics of the treated soils. A third type of remediation technique is the in situ immobilization of the metals using sequestering agents such as minerals (e.g., apatite, zeolite) or industrial byproducts (e.g., steel shots). This third type of approach is an attractive alternative to many current remediation methods, especially for large industrial areas and dumping grounds. Immobilization of metals reduces both leaching and plant bioavailability. Experiments have been carried out using highly soluble forms of phosphate (P, e.g. K_2HPO_4 , DAP) (Hettiarachchi et al., 2001). Soluble P added to contaminated soil can induce the formation of pyromorphite, which has very low solubility. However, the addition of highly soluble P increases the risk of eutrophication due to the application of large quantities of such amendments. Laboratory trials using phosphate rock (PR) have also been successful (Basta and McGowan, 2004; Zhu et al., 2004), but PR apatite is highly insoluble and so might not release P sufficiently rapidly to remediate contaminated soil within an acceptable time scale. Using finely powdered synthetic hydroxyapatite in soils and solutions results in the formation of pyromorphite (Nriagu, 1984; Zhang and Ryan, 1999; Basta and McGowan, 2004), but the use of synthetic hydroxyapatite on a field scale is economically unfavorable.

It has recently been suggested that poorly crystalline apatite, such as bone char apatite, might represent a low-cost, readily available phosphate source that could be used to remediate metal-contaminated soils without causing excessive P runoff (Ma et al., 1995; Ma and Rao, 1997). Bone char is a mixed compound adsorbent in which carbon is distributed throughout a porous structure of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$ or CaHAP). It contains around 76% of CaHAP, which is not only

a major inorganic constituent of teeth and bones but also the main inorganic constituent of phosphate rock (Cheung et al., 2001). The physical and chemical properties of the CaHAP have been widely reported; the removal mechanism has been suggested to be not only an adsorption effect but also a type of ion-exchange reaction between the ions in solution and the calcium ions of the apatites (Danny et al., 2004). However bone char application to metal-contaminated soils has rarely been reported. In this form, the major compound, CaHAP, in bone char has been developed as a treatment for decontaminating polluted water (Gabaldon et al., 1996; Dabbi et al., 1999; Wilson et al., 2001). In particular, its potential to adsorb both cationic and anionic metal species including radionuclides from radioactive wastes and contaminated water supplies is now being examined. Recently, the ability of bone meal addition to immobilize pollutant metals in soils has also been reported (Hodson et al., 2000). In the present study, bone char was used in pot experiments and sequential extraction was employed to investigate the effects of bone char application on bioavailability of Pb in a smelter-contaminated soil from Hunan Province, south China. The aim of this study was therefore to examine the changes in Pb speciation in soils after treatment with bone char and to determine whether bone char additions could be a feasible remediation treatment for soils contaminated with Pb.

2. Materials and methods

2.1. Experimental soil and amendments

Soil (0–30 cm in depth), characterized as a haplic acrisol according to the FAO soil taxonomy, was collected from a suburban area (both for residents and vegetable production) in Changsha City (111°53′–114°15′E, 27°51′–28°41′N), the capital of Hunan Province, south China. The soil was polluted with heavy metals due to local smelting industry. The soil sample was air-dried and ground to pass a 1-mm nylon sieve. About 1.0 g of homogenized soil samples were digested with 12.5 mL of aqua regia ($HNO_3:HCl:HClO_4 = 3:1:1$). The samples were heated until the color became clear, dissolved with several drops of 1% HNO_3 , filtered, diluted to a volume of 50 mL with distilled water, and analyzed for the total content of Cd, Pb, Zn and Cu (NISS-CAS, 1981). Soil pH was determined in 1:2.5 soil/water suspensions after 0.5 h with a combination pH electrode. Soil organic matter was determined by wet digestion with $K_2Cr_2O_7/H_2SO_4$; the conversion factor for organic carbon into organic matter was taken as 1.724. Available P was extracted with $0.5 \text{ mol L}^{-1} NaHCO_3$, and the other properties of the soil were determined according to standard methods recommended by the

Table 1
Some basic properties of the soil studied

pH (H ₂ O)	Organic matter	Mechanical composition (g kg ⁻¹)				Total ^a (mg kg ⁻¹)			Available (mg kg ⁻¹)		
		<0.001 mm	<0.002 mm	<0.01 mm	<0.05 mm	Cd	Pb	Zn	N	P	K
7.06	29.67	68.32	120.45	248.46	389.66	6.6	313.2	604.9	20.1	27.7	88.6

^a The critical values of the soil environmental quality standard in China (GB 15168-1995) were total Cd 0.3 mg kg⁻¹, total Pb 250 mg kg⁻¹ and total Zn 150 mg kg⁻¹.

Chinese Society of Soil Science (Lu, 1999). Some basic physio-chemical properties of the soil and the concentrations of a range of elements in this soil and amendments used are listed in Table 1. Concentrations of Cd, Pb and Zn in the soil greatly exceeded those of the soil environmental quality standards in China, so the soil was regarded as heavily metal-contaminated.

2.2. Bone char

The natural bone char used in this study was commercially manufactured and purchased from Brimac 216 (Brimac Charcoals Limited in the UK) and SDF Co., Ltd., Zhejiang Province, China, respectively. The composition of the bone char from Brimac and Zhejiang Province includes: hydroxyapatite, 72, 76 wt %; CaCO₃, 7.2, 7.9 wt %; acid insoluble ash, 2.1, 2.3 wt %, respectively. The products were ground and sieved to 220-mesh size (<80 µm). Deionized water was used for making metal solutions and washing. The chemicals used for this study were all of reagent grade.

2.3. Treatments

The experiment was conducted in a greenhouse with 9 treatments: (1) control treatment (CK), no amendment added; (2) bone char from the UK treatment (E) at 4 rates, 2.0 (E-1), 4.0 (E-2), 8.0 (E-3), and 16.0 (E-4) g kg⁻¹ soil and (3) bone char from China (C) at 4 rates, 2.0 (C-1), 4.0 (C-2), 8.0 (C-3), and 16.0 (C-4) g kg⁻¹ soil. Experimental pots were arranged in a fully randomized design with four replicates. Each plastic pot was evenly filled with 1 kg soil and different dosages of amendments. Nitrogen (N) and potassium (K) were applied as basal nutrients in the form of solution to each pot at rates of 0.2 g N kg⁻¹ soil as ammonium sulfate and 0.125 g K kg⁻¹ as potassium chloride. Each treated soil was incubated at 60% water holding capacity at 25 °C for 25 days. Then, pre-germinated seeds of Chinese cabbage (*Brassica chinensis* L.) were planted in each pot. Pots were watered with deionized water according to water loss by weighing. Plants were grown in a greenhouse for two months with temperatures between 20 and 25 °C in autumn in Beijing, China. At harvest, the shoots and roots were sampled, washed with water, and oven-dried at 70 °C for 24 h, then ground to pass a 40 µm sieve.

2.4. Metal analysis

Sub-samples of the powdered plant (1 g dry matter) were digested overnight in 14 M HNO₃ (5 mL) and HClO₄ (5 mL) and heated at 140 °C for 2 h (Lu, 1999). The digests were filtered with a Whatman No. 42 filter paper and diluted to 25 mL. Concentrations of Pb in the digests were determined by inductively-coupled plasma optical emission spectrometry (ICP-OES) (Optima 2000, Perkin Elmer Co. USA). The detection limit of Pb was 0.01 mg L⁻¹. A geochemical standard reference soil (GSS-6) (GBW-07406, China National Center for Standard Materials) was used as a certified reference material. Certified concentrations in the reference material never differed by more than 10% from the measured concentrations. At harvest, soil pH was also measured in water (soil/water = 1:2.5) by a glass electrode (Lu, 1999).

The method of sequential extraction developed by Tessier et al. (1979) was employed in this study. Each of the chemical fractions is operationally defined as follows:

- Exchangeable: 1 g soil (dry wt.) was extracted with 8 mL of pH 7, unbuffered, 1.0 M MgCl₂ in polyethylene centrifuge tubes for 1 h at 25 °C with continuous agitation.
- Carbonate: residue from the exchangeable fraction was extracted with 8 mL of pH 5, 1.0 M NaOAc for 6 h at 25 °C with continuous agitation.
- Fe/Mn oxide: residue from the carbonate fraction was extracted with 8 mL of 0.04 M NH₂OH·HCl in 25% acetic acid (v/v) for 6 h at 96 °C with occasional agitation.
- Organic: residue from the Fe/Mn oxide fraction was extracted with 2 mL of 0.02 M HNO₃ and 3 mL of pH 2, 30% H₂O₂ for 2 h at 85 °C with occasional agitation, an additional 3 mL of pH 2, 30% H₂O₂ for 3 h at 85 °C with occasional agitation, and then 3 mL of 3.2 M NH₄OAc in 20% HNO₃ (v/v) was added and agitated continuously for 0.5 h at 25 °C.
- Residual: residue from the organic fraction was removed into beakers and digested with HNO₃–HClO₄.

After each extraction, separation was performed by centrifugation at 10,000 rpm for 20 min. Metal

concentrations in the soil solutions were determined by ICP-OES as in plant digests.

Data were analyzed using the SAS software package (SAS Institute, 1985). The means were compared using the least significant difference (LSD) ($P \leq 0.05$).

2.5. X-ray diffraction (XRD) analysis

Clay fractions of selected soil samples were separated by centrifugation and characterized using X-ray diffraction (XRD, X'pert PRO MPD, Panalytical, Co.) to identify the possible newly formed Pb-phosphates. Air-dried clay fractions of the soil samples were sieved to an effective diameter of $\leq 40 \mu\text{m}$ before XRD analysis. The samples were measured using a continuous scanning technique from 10 to $90^\circ 2\theta$ with Cu K α a radiation on a computer-controlled diffraction meter equipped with stepping motor and a scan speed of $2^\circ 2\theta$ per minute.

3. Results and discussion

3.1. Effect of amendments on the growth and uptake of Pb

Shoot biomass production averaged 4.0 g pot^{-1} on a dry weight basis (Table 2). No amendment significantly changed shoot and root biomass production of Chinese cabbage (*B. chinensis* L.), except that in E-4 and C-4 treatments shoot biomass was higher than in the control treatment. Increasing the application of bone char (at rates of 4 g kg^{-1} and above) significantly reduced the concentrations of Pb in the shoots of Chinese cabbage grown in the contaminated soil (Table 3). Pb concentrations in roots decreased with increasing rates of bone char application. In the control treatment, mean Pb concentration in plant roots was 27.81 mg kg^{-1} , and it was reduced substantially to 6.72 and 8.42 mg kg^{-1} in the E-4 and C-4 treatments. In the

Table 2
Biomass production (g/pot DW) of Chinese cabbage (*Brassica chinensis* L.) grown in the control and bone char-treated soil^a

Treatments	Shoot	Root
CK	$3.62 \pm 0.10 \text{ cd}$	$0.74 \pm 0.05 \text{ a}$
E-1	$3.99 \pm 0.16 \text{ cd}$	$0.79 \pm 0.08 \text{ a}$
E-2	$4.06 \pm 0.21 \text{ bc}$	$0.78 \pm 0.06 \text{ a}$
E-3	$4.23 \pm 0.30 \text{ abc}$	$0.81 \pm 0.03 \text{ a}$
E-4	$4.43 \pm 0.22 \text{ ab}$	$0.80 \pm 0.05 \text{ a}$
C-1	$4.22 \pm 0.33 \text{ abc}$	$0.75 \pm 0.02 \text{ a}$
C-2	$4.33 \pm 0.35 \text{ abc}$	$0.79 \pm 0.06 \text{ a}$
C-3	$4.22 \pm 0.13 \text{ abc}$	$0.74 \pm 0.03 \text{ a}$
C-4	$4.50 \pm 0.31 \text{ a}$	$0.79 \pm 0.04 \text{ a}$

^a Mean $\pm$ SD ($n = 4$) with the same letters in the same part of plants are not significantly different at $p < 0.05$. CK, control; E-1, UK bone char level-1 (E-1); C-1, Chinese bone char level-1 (C-1), and so on.

Table 3

Tissue Pb concentrations (mg kg^{-1}) of Chinese cabbage (*Brassica chinensis* L.) grown in smelter-contaminated soil in pot culture receiving various bone char amendments^a

Treatments	Shoot	Root
CK	$4.45 \pm 0.06 \text{ a}$	$27.81 \pm 0.70 \text{ a}$
E-1	$3.85 \pm 0.11 \text{ a}$	$23.24 \pm 1.29 \text{ b}$
E-2	$3.61 \pm 0.62 \text{ b}$	$14.86 \pm 0.83 \text{ c}$
E-3	$3.31 \pm 0.27 \text{ c}$	$7.75 \pm 0.46 \text{ d}$
E-4	$1.97 \pm 0.10 \text{ d}$	$6.72 \pm 0.51 \text{ d}$
C-1	$4.13 \pm 0.13 \text{ a}$	$23.65 \pm 0.82 \text{ b}$
C-2	$3.96 \pm 0.05 \text{ b}$	$16.84 \pm 0.72 \text{ c}$
C-3	$3.01 \pm 0.11 \text{ c}$	$8.75 \pm 0.92 \text{ d}$
C-4	$2.04 \pm 0.07 \text{ d}$	$8.42 \pm 0.53 \text{ d}$

^a Mean $\pm$ SD ($n = 4$) column with the same letters in the same part of grass are not significantly different at $p < 0.05$. CK, control; E-1, UK bone char level-1 (E-1); C-1, Chinese bone char level-1 (C-1), and so on.

treatments of E-4 and C-4, the Pb concentrations in shoots were only 24.1%, 30.2% and 44.0%, 45.3% of the control treatment, respectively. The efficiency of the bone char from the UK was similar to that of from Zhejiang Province, China in reducing Pb uptake by Chinese cabbage. The national food safety standard for Pb (dry weight basis) in leafy vegetables is 0.4 mg kg^{-1} (GB14935-94, in China). Although the amendment treatments reduced the uptake of Pb (1.97 mg kg^{-1}) by the Chinese cabbage grown in the metal-contaminated soil, in order to produce vegetables with Pb concentrations under the national food safety level, higher rates of bone char application might be needed.

3.2. Speciation of soil lead (Pb)

Lead bioavailability is assumed to depend largely on the chemical forms in which soil Pb is incorporated. In this study, substantial amounts of Pb were found in the organic and Fe/Mn oxide fractions (55.4% of the total Pb) in the control treatment, which was probably due to the fact that Pb^{2+} has a strong affinity for humic acid and complexes with organic matter to form stable Pb–humic acid complexes. The small amounts of Pb in exchangeable forms suggest that the solubility and mobility of this element were very low in the soil. After 85 days incubation with bone char addition, the exchangeable forms of Pb in the soil with each treatment decreased compared with the unamended treatment (Fig. 1), but they only decreased substantially in the E-4 and C-4 treatments. In all treatments, the exchangeable fraction, the carbonate and Fe/Mn bound forms and organic forms of Pb decreased, but the carbonate form to a relatively lesser extent. The water-soluble form of Pb was not detectable ($< 0.01 \text{ mg kg}^{-1}$) in the soil with all treatments including the unamended control. The E-3, E-4, C-3 and C-4 treatments significantly changed Pb levels from non-residual (sum of the exchangeable

Fig. 1. Percentages of Pb in each fraction of the soils with different treatments: no amendment (CK), UK bone char level-1 (E-1), Chinese bone char level-1 (C-1), and so on. Exch. = water soluble and exchangeable; Carb. = carbonate; Fe/Mn = Fe/Mn oxide; OM = organic matter; Resid. = residual.

fraction, the carbonate form, the Fe/Mn oxide and the organic form fraction) to residual forms (Fig. 1), the residual fractions in E-4 and C-4 treatments increasing from 39.2% in the control treatment to 82.8% and 82.7%, respectively. The organic forms of Pb in soil were reduced to a relatively greater extent with all treatments compared with the unamended control. Changes in organic forms may indicate Pb immobilization by the charcoal fraction of bone char. Since the major components in bone char are hydroxyapatite and CaCO_3 , hydroxyapatite is not just a source for adsorption but also enables ion-exchange to occur (Ma et al., 1995), so the chemisorption by hydroxyapatite and ion-exchange may be a dominant mechanism for the transformation of Pb from non-residual forms to residual fractions, because these adsorption processes could be essentially irreversible. The most effective

Fig. 2. Relationship between tissue Pb concentrations and Pb fractions in the soil after 85 days incubation. (a) Shoot Pb concentrations vs. exchangeable Pb fraction; (b) root Pb concentrations vs. exchangeable Pb fraction; (c) shoot Pb concentrations vs. residual Pb fraction; (d) root Pb concentrations vs. residual Pb fraction.

amendments for transforming the non-residual forms of Pb to the residual forms were found to be in the E-4 and C-4 treatments in this study. However, further experiments are needed to determine the optimum application rate.

3.3. Relationship between Pb speciation and plant uptake

It has been reported that heavy metal accumulations in plants are determined not only by their total concentrations in soils, but more importantly by the physico-chemical properties of the soil and the metal of concern. Further investigation into the effects of chemical forms of Pb on its uptake revealed that exchangeable form of Pb in soil exhibited strong influence on its uptake than the total Pb concentration in soil (Fig. 2). Correlation coefficients suggested that there were positive correlations between Pb concentrations in plant tissues (both shoots and roots) and exchangeable fractions in the soil. Conversely, Pb concentrations in shoots and roots presented negative correlations with the residual forms of Pb in the soil. These results verified the inference that its chemical forms related to solubility in soil determine Pb bioavailability.

3.4. X-ray diffraction

Analysis of mineralogical changes resulting from the application of bone char using XRD helps to better understand the mechanism of Pb immobilization in the soil. The XRD patterns of the bone char-treated and control soils are shown in Fig. 3. The distinctive higher peaks at 3.22 Å (left) and 2.96 Å (right) in the treated soil samples (E-4, C-4) than the control suggested in situ formation of lead phosphate ($\text{Pb}_2\text{P}_4\text{O}_{12}$) and lead hydroxyapatite-like minerals ($\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$) 85 days after bone char application. In this study, the phosphate source could possibly come from the release of P from the major compound CaHAP in bone char. The lower peaks in the control soil suggested there were some amounts of lead phosphate and lead hydroxyapatite-like minerals existing in the unamended soil; the addition of bone char enriched the formation of these compounds in the soil. Similarly, Ma et al. (1995) and Laperche et al. (1997) observed a peak at 2.96 Å upon P addition to a Pb-contaminated soil. Thermodynamic considerations predict that Pb phosphate minerals are the most stable among Pb compounds (Laperche et al., 1996; Seaman et al., 2003). Thus, they can be readily formed in the presence of adequate Pb and P. Ruby et al. (1994) also demonstrated that the weathering of galena (PbS) to insoluble lead phosphates occurred in soils at a port facility historically used for shipment of phosphate.

3.5. Effects on soil pH

A significant percentage of calcium carbonate (CaCO_3) gives bone char alkaline properties. Whilst the addition of bone char did not significantly change soil pH compared to the unamended control after 85 days (this incubation period included the initial 25 days without plant and the latter 60 days with plant) in this study, the soil pH values of each treatment were only slightly higher than that of unamended treatment (Fig. 4) except at the highest application rates. This result agrees with those reported by Cheung et al. (2001), and Hodson et al. (2000). However, the pH values of both E-4 and C-4 treatments were the highest among the treatments (Fig. 4). The change in soil pH was an additional mechanism of bone char-induced reduction in Pb bioavailability, since pH is one of the most important parameters affecting Pb bioavailability to plants (Cotter-Howells, 1996).

4. Conclusions

The addition of bone char to a Pb-contaminated soil resulted in a reduction in exchangeable amounts of Pb in the soil and an increase in the pH of the soil pore water and the soils. No amendment significantly changed the shoot or root biomass production of Chinese cabbage, except that in E-4 and C-4 treatments shoot biomass was higher than the control treatment. In the plant tissues, a gradual decrease in Pb uptake was observed

Fig. 3. XRD patterns of selected soils with the highest addition of bone char after 85 days incubation. CK, the control; E-4, UK bone char level-4; C-4, Chinese bone char level-4; LP, lead phosphate; LHAP, lead hydroxyapatite.

Fig. 4. pH changes in the tested soil as affected by different amendments. Symbols are same as in Fig. 1.

with increasing bone char application rate. Batch experiments and subsequent extraction of Pb from controls and bone char amended soils indicated that bone char additions reduced the bioavailability of the Pb in the soil. X-ray diffraction of the bone char-treated soil at the end of the experiment revealed that Pb was associated with phosphorus as Pb-phosphates. Bone char amendments do appear to have potential as a remediation treatment for Pb-contaminated soils and more detailed studies are needed to explain the Pb-uptake response on the treated and untreated soils, in particular with application rate higher than 1.6%.

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