

The effect of grain size of rock phosphate amendment on metal immobilization in contaminated soils

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Abstract

When rock phosphates (RP) are used to remediate Pb-contaminated soils, their effectiveness is likely affected by their grain size. In this study, the effect of grain size of rock phosphate on the effectiveness of heavy metal immobilization in two contaminated soils was measured in pot experiment. Rock phosphate was used with four different grain sizes: <35, 35–72, 72–133 and 133–266 μm . The application rate of rock phosphate in two soils was determined based on P/metals (Pb, Zn, Cu and Cd) molar ratio of 5.0 in the soils. The results showed that rock phosphate of the smallest grain size (<35 μm) was superior to all of other grain sizes more than 35 μm for reducing uptake in plant (*Brassica oleracea* L.) shoots for Cd (19.6–50.0%), Pb (21.9–51.4%) and Zn (22.4–34.6%), respectively, as compared with the soil without application of rock phosphate. Sequential extraction analysis indicated that rock phosphate was most effective for soil Pb to induced transformation from non-residual fractions to a residual fraction than that for Zn and Cd. Such transformation was probably through dissolution of Pb associated with exchangeable (EX), organic fraction (OC), acidic fraction (AC) and amorphous Fe and Al oxides-bound (OX) fraction and precipitation of pyromorphite-like minerals. Results suggested that the rock phosphate with small grain size was superior to that with large grain size for in situ remediation technology. © 2005 Elsevier B.V. All rights reserved.

Keywords: Heavy metals; Immobilization; Rock phosphate; Grain size

1. Introduction

Addition of phosphate (P)-based materials to soils has proven to be extremely effective as a chemically immobilizing amendment for Pb-contaminated soils. Recently, this P-based approach to the remediation of Pb-contaminated soils has been widely used [1–3]. This technique is of particular interest because of its cost-effectiveness and less disruptive nature [4,5]. Significant effort has been made to evaluate the effectiveness of P on in situ remediation of contaminated soils and waters [6–10]. Phosphate minerals, i.e. rock phosphate (RP) and hydroxyapatite, have been shown to effectively immobilize Pb from various contaminated soils and waters [1,11–13]. In addition to reducing metal solubility, rock phosphate amendments are also effective in reducing metal bioavailability associated with incidental ingestion of soil by humans [14,15] and for reducing phytoavailability of heavy metals [9,16,17]. Takeuchi and Arai [18] suggested that Pb

immobilization resulted from the formation of a more stable lead phosphate, such as $\text{Ca}_{(10-x)}\text{Pb}_x(\text{PO}_4)_6(\text{OH})_2$ via an ion exchange mechanism where aqueous Pb replaces Ca on the hydroxyapatite lattice. Ma et al. [11], on the other hand, proposed the dissolution of rock phosphate and subsequent precipitation of a pyromorphite-like mineral ($\text{Pb}_{10}(\text{PO}_4)_6\text{X}_2$, $\text{X}=\text{OH}^-$, Cl^- , F^- , etc.) as the primary mechanism. Thus, the solubility and grain size of rock phosphate can affect the effectiveness of the amendment for in situ remediation technology. Therefore, the objective of this study was: (1) to compare the effectiveness of four grain size fractions of rock phosphate to reduce heavy metals (Cd, Pb and Zn) uptake by plant and (2) to investigate the fractionation of Pb in two smelter-contaminated soils after the addition of rock phosphate with four grain sizes.

2. Materials and methods

2.1. Materials

Surface soils (0–30 cm in depth) with elevated concentrations of Cd, Pb, Zn and Cu (Table 1) were collected from an urban

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Table 1
Some basic soil properties

Soil type	pH (H ₂ O)	Organic matter (g kg ⁻¹)	CEC (C mol kg ⁻¹) ^a	Mechanical composition (%)			Total ^b				Available ^b		
				Clay	Silt	Sand	Cd	Pb	Zn	Cu	N	P	K
Soil I	6.85	29.67	19.5 ± 2.5	36	33	31	6.6	338.8	637.9	56.7	20.1	27.7	88.6
Soil II	7.86	16.7	12.8 ± 3.2	42	39	19	4.5	275.6	328.78	36.5	7.7	24.2	38.9

^a Cation exchangeable capacity, mean ± S.D. (*n* = 4).

^b Unit: mg kg⁻¹.

area (both for residents and vegetable production) in Changsha, Hunan Province in Southeastern China (hereafter as Soil I) and suburban area in Fuyang, Anhui Province in East China (hereafter as Soil II). The soils were contaminated with heavy metals due to local smelting industries. The soil samples were air-dried and then ground to pass through a 2-mm sieve prior to use for pot experiment. Soil pH (soil:water; 1:2.5) was determined by a combination electrode. Particle size analysis was carried out using the hydrometer method. The suspension of soil (50 g) was prepared by boiling with 50 mL solution of 0.25 mol L⁻¹ Na₂C₂O₄. The suspension was diluted to 1 L in a 1-L cylinder. After mixing thoroughly, the hydrometer was placed in the cylinder to measure specific gravity after different times of settlement [19]. The properties of the soils were determined according to standard methods recommended by the Chinese Society of Soil Science [19]. Total concentrations of heavy metals of the soils was determined using digestion of soil sample (1.0 g) in 12.5 mL of aqua regia (HNO₃/HCl/HClO₄, 3:1:1). The samples with aqua regia were heated until the color became clear, diluted to a volume of 50 mL with distilled water. The concentration of heavy metals in the digestion was analysed by inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 2000, Perkin-Elmer Co., USA) for the total content of Cd, Pb and Zn [19]. The soil organic carbon was determined by wet digestion with K₂Cr₂O₇/H₂SO₄, the converting factor of organic carbon into organic matter was 1.724. Available P was extracted with 0.5 mol L⁻¹ NaHCO₃ and the other properties of the soil were determined according to standard methods recommended by the Chinese Society of Soil Science [19]. Some basic physiochemical properties of the soils are listed in Table 1.

2.2. Treatments

Mineral rock phosphate (21% P content) was provided by Yichang Fertilizer Co. Ltd., China. The sample of RP was sieved through 35, 72, 133 and 266 μm, respectively, before application. The RP material did not contain toxic metals except that

RP contained 2.3 mg kg⁻¹ Cd. For pot experiment, 19.2 g RP for Soil I and 11.7 g RP for Soil II with the above four grain sizes were mixed thoroughly with the soil before potting. Nitrogen and potassium fertilizers were applied in solution at a commonly used rate of 60 kg ha⁻¹ of N (as (NH₄)₂SO₄) and K₂O (as KCl). Rock phosphate application rate was based on the specific P/total metal molar ratio (5.0). Total metals, for the purpose of the immobilization treatments in this study, were defined as the sum of total Cd, Pb, Zn and Cu determined by inductively coupled plasma optical emission spectrometer. This application rate was chosen with the intent to immobilize the total concentrations of the main four metal species in the smelter-contaminated soils. Previous research has used the ratio of 3/5 P/M total as the basis of hydroxyapatite and apatite treatments to lead-contaminated soils [9,10,12,14]. This ratio corresponds to the P/Pb ratio for chloropyromorphite [Pb₅(PO₄)₃Cl]. However, due to the solubility of RP in soils, since the total P may not react with insoluble Pb, higher P/Pb molar ratios (up to 11.2) have been suggested by Zhang and Ryan [14], Basta and Gradwohl [20] and Hettiarachchi and Pierzynski [13].

2.3. Pot experiments

Two kilograms of the treated and untreated soil were packed into each pot. Five treatments were: a control with no amendment (T0), amendments with RP of grain size 133–266 μm (T1), 72–133 μm (T2), 35–72 μm (T3) and <35 μm (T4). There were four replicates for each treatment. The pots were kept moist (12%, w/w) for 4 weeks in a greenhouse. Ten-day-old seedlings of cauliflower (*Brassica oleracea* L.) were transplanted into the soil and thinned to four per pot on day 21 and kept in the greenhouse (with natural light) until harvest. Plants were harvested at 75-day-old.

At harvest, the plant shoots and roots were removed from the soils, washed with deionised water, oven-dried (48 h at 70 °C) and weighed until reached constant weight. Samples of dry matter (DM) were digested using HCl/HNO₃/HClO₄ (3:2:1, v/v/v)

Table 2
Procedure for the sequential extraction of metals from the soils and corresponding phases

Phase/association	Abbreviation	Step	Operational definition
Exchangeable	EX	1	16 mL 1 M MgCl ₂ , pH 7.0, shaking 1 h
Organic-bound	OB	2	40 mL 1 M Na ₄ P ₂ O ₇ , shaking 24 h
Acidic	AC	3	16 mL 1 M NaOAc, pH 5.0 with HOAc, shaking 5 h
Amorphous Fe and Al oxides-bound	OX	4	40 mL 0.175 M (NH ₄) ₂ C ₂ O ₄ /0.1 M H ₂ C ₂ O ₄ , shaking 4 h in the dark
Residual	RES	5	Acid mixture ^a

^a The residue from step 4 was digested in 15 mL HCl/HNO₃/HClO₄ (3:1:2, v/v/v) at 150 °C.

and the concentrations of Cd, Pb and Zn were determined by ICP-OES. Soil samples were air-dried for analysis. Standard reference materials of soil (GSS-6, GBW-07406, China National Center for Standard Materials) and plant (GSV-4, GBW07605, tea leaves) in analytical procedure were used for quality control.

2.4. Chemical extraction

A sequential extraction was performed for soil samples from each pot after air-dried (1.00 g in 40-mL polyethylene centrifuge tubes) according to the scheme of the modification of the Tessier's sequential extraction method proposed by Elliot et al. [21]. The order of the extraction was changed to leach the metal bound to the organic phase before dissolving the carbonate and iron oxide phases. This allows the destruction of organic phases, which may entrap the mineral materials and thus provide a better extraction for the following phases (Table 2). A reference soil material (as above) was used to compare metal recovery based on sequential extraction with certified values and the recoveries were satisfactory for all metals investigated.

2.5. Statistical analyses

The data were subjected to ANOVA analysis by using SPSS Version 12.0 software (SPSS Inc., USA) and differences ($p < 0.05$) between means were determined using the Duncan–Waller test.

3. Results and discussion

3.1. Effect on the plant biomass and the uptake of Cd, Pb and Zn

No significant difference in plant biomass between treatments, except that for Soil I T4 had higher root and shoot biomass compared to the control, and that for Soil II T4 had higher shoot biomass compared to the control (Table 3). Gen-

erally, the biomass in Soil I was more than that in Soil II. The application of phosphate amendments tended to decrease the toxicity of heavy metals in these two soils, but the differences in biomass did not come to the levels of significance except for T4 treatment (Table 3).

Table 3
Biomass of cauliflower (*Brassica oleracea* L.) grown in the contaminated soils with different grain sizes of RP amendments

Treatment	Shoot (g pot ⁻¹ DW)	Root (g pot ⁻¹ DW)
Soil I		
T0	5.09 ± 0.14 b	0.74 ± 0.09 b
T1	5.20 ± 0.28 b	0.84 ± 0.12 b
T2	5.33 ± 0.19 b	0.85 ± 0.07 b
T3	5.34 ± 0.25 b	0.84 ± 0.11 b
T4	5.69 ± 0.22 a	1.16 ± 0.16 a
Soil II		
T0	3.75 ± 0.16 b	0.70 ± 0.01 a
T1	3.84 ± 0.32 b	0.74 ± 0.07 a
T2	3.79 ± 0.17 b	0.68 ± 0.04 a
T3	4.00 ± 0.24 ab	0.77 ± 0.11 a
T4	4.27 ± 0.26 a	0.79 ± 0.08 a

Mean ± S.D. ($n = 4$), columns with the same letters (a and b) in the same part of plants are not significantly different at $p < 0.05$. T0, without amendment; T1, receiving RP amendment of grain size 133–266 μm ; T2, 72–133 μm ; T3, 35–72 μm ; T4 <35 μm , respectively.

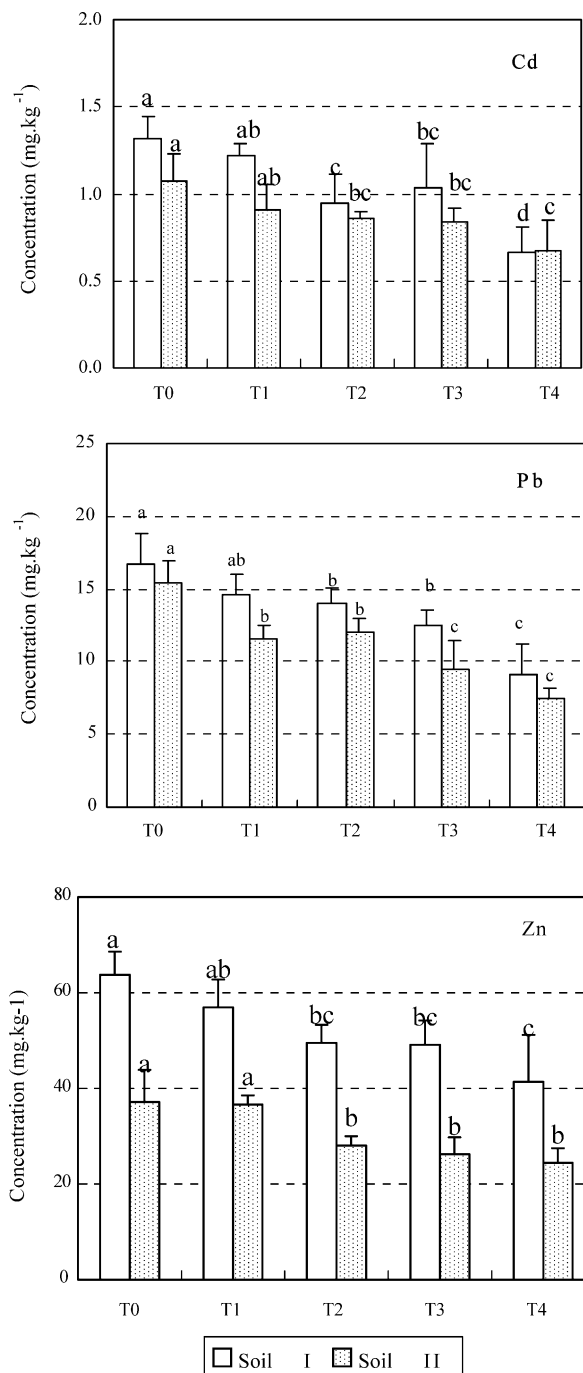


Fig. 1. The concentrations of Cd, Pb and Zn in the shoots of cauliflower (*Brassica oleracea* L.) grown in metal-contaminated soils in pot culture receiving different grain size of the same RP amendments (mg kg^{-1}). ^aMean + S.D. ($n = 4$); T1, receiving RP amendment of grain size 133–266 μm ; T2, 72–133 μm ; T3, 35–72 μm ; T4 <35 μm , respectively, column with the same letters in the same soil are not significantly different at $p < 0.05$. Open columns are for Soil I and dotted ones for Soil II.

After 110 days incubation period, soil pH values after the amendment of PR varied from 6.9 to 7.11 in Soil I and 7.80 to 8.0 in Soil II, respectively, and this change in pH was considered to be negligible. The concentrations of Cd, Pb and Zn in cauliflower shoots were much lower than in roots (Figs. 1 and 2). In the treatments (T2–T4) where RP was applied in grain size $<133\ \mu\text{m}$, the concentrations of Cd, Pb and Zn in shoots were significantly lower than in the control for both soils (Fig. 1), the reduction in concentrations of Cd, Pb and Zn in the shoots ranged from 19.6 to 50.0% for Cd, 21.9 to 51.4% for Pb and 22.4 to 34.6% for Zn, respectively. The concentrations of Cd, Pb and Zn in plant shoots decreased with the decreasing grain sizes, and the best effect was observed in T4 treatment. However, T1 (133–266 μm) treatment had marginal effect on the concentrations of Cd and Zn in Soil II.

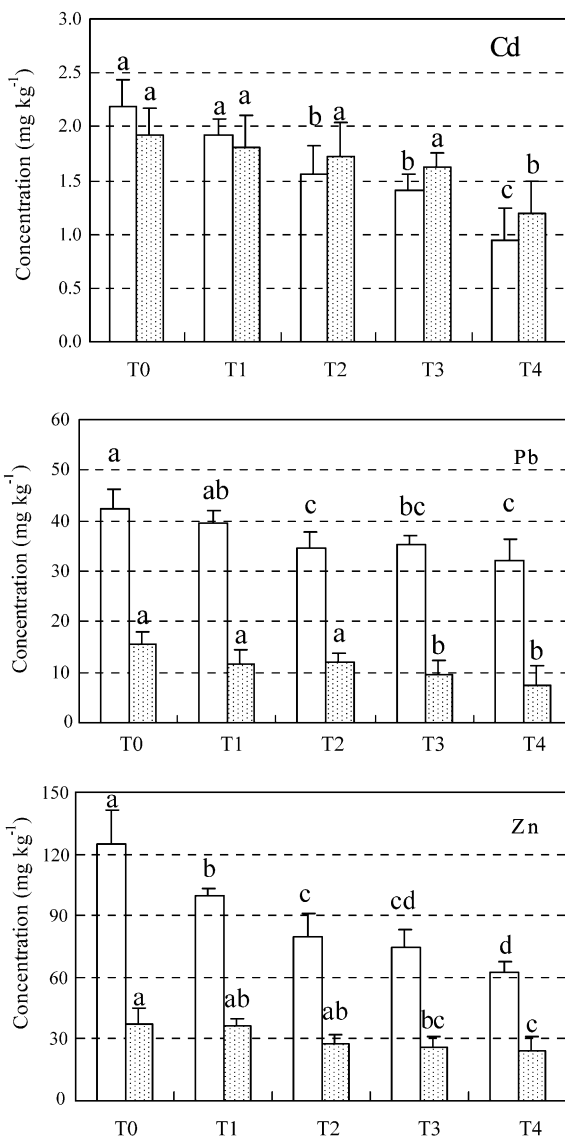


Fig. 2. The concentrations of Cd, Pb and Zn in the roots of cauliflower (*Brassica oleracea* L.) grown in metal-contaminated soils in pot culture receiving different grain size of the same RP amendments (mg kg^{-1}). ^aMean + S.D. ($n=4$); column with the same letters in the same soil are not significantly different at $p < 0.05$. Open columns are for Soil I and dotted ones for Soil II; for abbreviations, see Fig. 1.

This effect was similar to that observed with the concentrations in plant roots. The result indicated that the grain size of RP could significantly ($p < 0.05$) influence Cd, Pb and Zn concentrations in the vegetable plant shoots and roots. However, it is important to point out that although the phosphate amendments significantly reduce the concentration of metals in plants and therefore the potential transfer of metals in the food chain, this reduction is not sufficient to produce foodstuffs that meet the quality standards of heavy metal concentrations in China. In both soils the concentration of Cd and Pb in the vegetable in all treatments and Zn in some treatments still exceeded the maximum permitted concentration in foodstuff of 0.1, 0.4 and 50 mg kg^{-1} of dry weight [29].

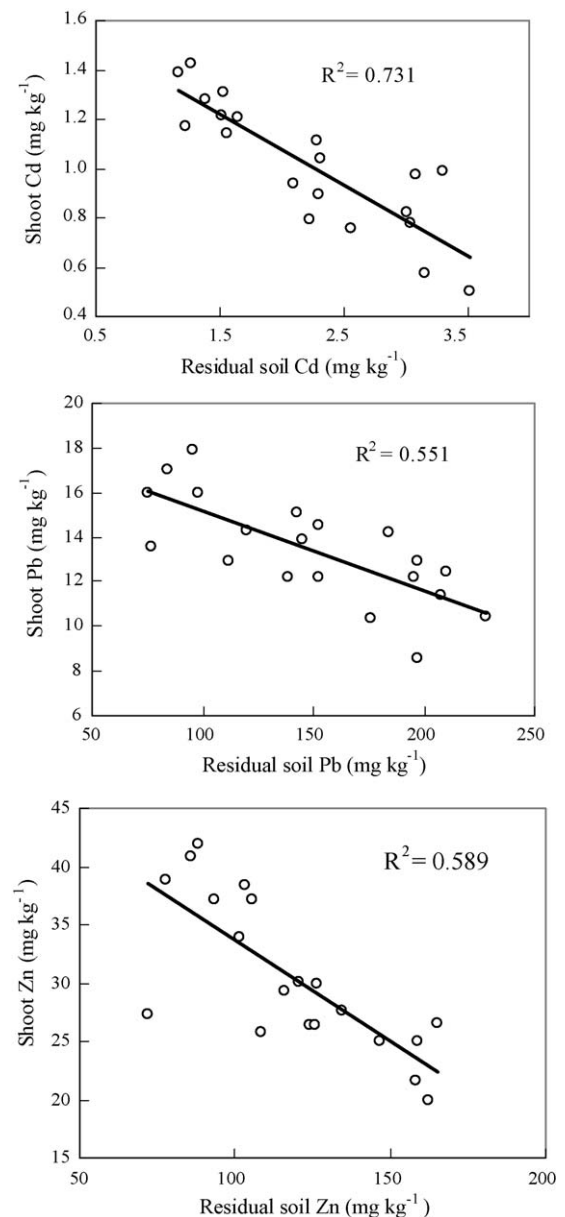


Fig. 3. Relationship between residual soil metals (Cd, Pb and Zn) and shoot metals concentration after harvest.

Table 4
Relative percentages (%) of Cd, Pb and Zn in the total fraction (non-residual) of EX, OB, AC and OX (A + B + C + D) and fraction of residual (E) in the unamended and treated soils

Treatment	Cd		Pb		Zn	
	A + B + C + D	E	A + B + C + D	E	A + B + C + D	E
Soil I						
T0	0.816	0.184 d	0.601	0.399 d	0.719	0.281 c
T1	0.760	0.240 c	0.492	0.508 c	0.661	0.339 bc
T2	0.645	0.355 b	0.380	0.620 b	0.611	0.389 b
T3	0.502	0.498 a	0.302	0.698 a	0.558	0.442 b
T4	0.499	0.501 a	0.298	0.702 a	0.461	0.539 a
Soil II						
T0	0.775	0.225 c	0.708	0.292 d	0.751	0.249 d
T1	0.722	0.278 c	0.564	0.436 c	0.682	0.318 c
T2	0.607	0.393 b	0.450	0.550 b	0.632	0.368 bc
T3	0.482	0.518 a	0.386	0.614 a	0.581	0.419 b
T4	0.467	0.533 a	0.362	0.638 a	0.488	0.512 a

For abbreviations, see Table 3. Means followed by the same letters (a–d) within a column are not statistically different at $p < 0.05$.

3.2. Sequential extraction study

The distribution of Cd, Pb and Zn in the soils of T0 and the RP-treated pots (T1–T4) is presented in Table 4. The metals (Cd, Pb and Zn) in the unamended pots were primarily associated with the non-residual fraction. The percentage of metals bound with the non-residual fractions accounted for over 76–82% for Cd, 60–71% for Pb and 72–75% for Zn, respectively, in the unamended soils, which indicated that a substantial fraction of Cd, Pb and Zn in the contaminated soil may be available for plant uptake. For RP-amended soil, RP treatments with grain size $< 133 \mu\text{m}$ all transferred non-residual fractions of Cd, Pb and Zn to the residual fraction (Table 4). Among the four treatments, T4 ($< 35 \mu\text{m}$) was the most effective in converting metals from the non-residual to the residual fraction, while the T1 treatment was the least effective, indicating that the potential bioavailability of Cd, Pb and Zn in RP treatments decreases with decreasing grain size. Although chemical extraction procedures suffer from a lack of phase specificity, it can provide an operational separation of metal forms with varying strength of binding to sediment and soil [22,23] and can be viewed as an inverse scale of the relative availability of metals. Sequential extraction schemes are widely used to evaluate the mobility and bioavailability of heavy metals in soils as well as the efficacy of decontamination amendment. Assuming the non-residual metal (sum of the exchangeable [EX], organic fraction [OC], acidic fraction [AC] and amorphous Fe and Al oxides-bound [OX]) is more bioavailable than the residual fraction, the effectiveness of in situ remediation of metal-contaminated soils can be assessed using a fractionation scheme [24]. The more effective treatments convert greater amounts of metal from the non-residual to the residual fraction.

The decrease in metal bioavailability can probably be attributed to the fact that more P was available for the formation of metal-phosphate from treatments with smaller grain size than from treatments with larger grain size. It was noted that RP amendment was less effective for the immobilization of Cd than for Pb and Zn. Solubility products of cadmium phosphate are

much greater than that of lead phosphate [25]. Therefore, lead phosphate was probably formed prior to Cd [26].

3.3. Relationship between residual soil metals and shoot metal concentrations

A negative correlation was observed between the concentrations of Cd, Pb and Zn in shoots and the residual concentrations of Cd, Pb and Zn in the soils (Fig. 3), and a positive correlation was observed between shoot metal concentrations and EX fractions (data not shown). This relationship is in agreement with the fact of great reduction in the total concentrations of EX, OB, AC and OX fractions in the treated soil. Similarly, positive correlations between extractable Cd in soil and Cd concentrations in tobacco leaves were reported by refs. [10,27,28]. In this study, RP amendments with grain sizes $< 133 \mu\text{m}$ resulted in a significant increase in residual fraction of Cd, Pb and Zn, which corresponded to the decrease in shoot concentrations of Cd, Pb and Zn. This is likely to be caused by the reduction in the availability of Cd, Pb and Zn in soils after RP amendment. Metals present in soil sediments may exist as constituent elements present in the essentially insoluble products of weathering (lattice-bound metals) or in a variety of secondary forms (exchangeable, organic matter-bound, carbonate-bound, Fe/Mn oxide-bound) which are more reactive and likely to be bioavailable [5]. Metal uptake by plants in phosphate-amended soils has often been correlated with some extractable fraction of the soil metal. In this study, phosphate amendment led to a dramatic increase in residual concentrations of Cd, Pb and Zn in the soils, which became more significant in the treated soils. Differences in the distribution of metal fractions between the two soils were likely to be affected by soil properties, especially soil organic matter content and pH. Compared with Cd and Zn, the residual fraction of Pb was much more in both soils (Table 4). This may be explained by differences in chemical characteristics between Cd, Zn and Pb. Future effort should be made to evaluate the potentiality of different sizes of RP in situ remediation of metal-contaminated soils, and to investigate the effect

of combining organic acids and microbial metabolism with RP to further increase soil P availability for metal immobilization in contaminated soils.

4. Conclusions

For the two smelter-contaminated soils, RP amendments with smaller grain size was more effective than larger grain size with respect to decreasing Cd, Pb and Zn bioavailability, as indicated by their uptake by cauliflower (*B. oleracea* L.) shoots and roots. Of the treatments investigated, T1 (133–266 μm) treatment was mostly ineffective in reducing Cd, Pb and Zn uptake by the plant, T4 (<35 μm) treatments were not only highly effective at reducing Cd, Pb and Zn uptake by the plant shoots and roots, but transformed large amounts of Cd, Pb and Zn from non-residual fraction to residual fraction, with increment of 30.8–31.7% of Cd, 30.3–34.6% of Pb and 25.8–26.3% of Zn, respectively, as when compared with the untreated soil. The results suggested that rock phosphate with smaller grain size was more effective to lower the bioavailability and increase the geochemical stability of soil metals than larger size, possibly due to its higher specific surface area.

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