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Effects of particle sizes of rock phosphate on immobilizing heavy metals in lead zinc mine soils

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Abstract

Phosphate-induced immobilization is recognized as one of effective in situ remediation methods for heavy metal contaminated soils. Phosphate-based minerals that adsorb, chelate, or complex heavy metals in soil were greatly concerned as effective heavy metals immobilizing materials. Effects of particle sizes of rock phosphate on immobilizing heavy metals in Pb-Zn mine soils by a greenhouse experiment was conducted. Rock phosphate was added to a Pb-Zn mine soil with four different particle sizes, D97<101.43 µm (UP), D97<71.12 µm (P1), D97<36.83 µm (P2) and D97< 4.26 µm (P3) (the diameters of 97% of the particles were less than 4.26 µm.), and 2 rates (2.5% and 5%). *Lolium prenne*, L. were grown in the treated soils. Compared to the control, addition of rock phosphate (RP) decreased metal contents in both roots and shoots significantly. Pb contents in shoots decreased by 19.59%-37.80% by different particle sizes at the rate of 5%, reaching lowest level at lowest particle size P3. Zn contents in shoots decreased by 13.47% -13.75 %, Cu in roots was decreased by 18.46%-67.98% and in shoots by 16.82%-32.61%, and Cd in roots decreased by 31.03%-74.23%. The results indicated that, RP can reduce the phytoavailability of Pb, Zn, Cu and Cd in soil significantly by immobilization and the effects strengthened with the decrease of particle size and increasing the rate of addition.

Keywords: Particle size, rock phosphates (RP), immobilization, heavy metals, Pb-Zn mine soil

1. Introduction

Heavy metal contamination of soil is a widespread global problem. Contaminated soil can be remediated by physical, chemical or biological techniques Generally, these techniques can be classified to two remediation strategies- extraction or stabilization. Stabilization is cost-effective and less disruptive to the soil and the environment. Stabilization of contaminants in soil can be achieved by addition of immobilizing amendments which are able to decrease metal leaching and bioavailability by inducing various sorption processes: adsorption to mineral surfaces, formation of stable complexes with organic ligands, surface precipitation and ion exchange (Kumpiene *et al*., 2008).

Phosphorus-containing amendments were greatly concerned amendments on in *situ* remediation of metal contaminated soils. Most of the studies were performed on stabilizing Pb in soils and mineral rock phosphate (RP) was particularly concerned because of its cost-effectiveness and less disruptive nature (Ma *et al.*, 1997; Hettiarachchi and Pierzynski, 2002; Cao *et al.*, 2004; Ownby *et al.*, 2005; Chen *et al.*, 2006; 2007; 2009), and the possible mechanisms of RP stabilizing Pb was suggested as a process including ion exchange processes at the surface of RP, surface complexation, and replacement of Ca in RP by Pb (Takeuchi and Arai, 1990; Jeanjean *et al.*, 1994; Ma *et al.*, 1995; Basta *et al*., 2001; Geebelen *et al*., 2002; Cao *et al.*, 2004) with formation of pyromorphite-type minerals [$Pb_5(PO_4)_3X$; X = F, Cl, B or OH]. For example, the formation of stable fluoropyromorphite [$Pb_{10}(PO_4)6F2$] was the main mechanism responsible for Pb stabilization in soil amended with RP containing F which dominated over surface sorption/complexation reactions(Cao *et al*., 2004).

Rock phosphate can also remove Zn and Cu from aqueous solutions (Xu *et al.*, 1994; Brown *et al.*, 2005). Cao *et al*. (2004) reported that sorption capacity of RP in multi-contaminated soil is in the order of Pb>Cu>Zn with sorption capacities of 138, 114, and 83.2 mmol/kg RP, respectively. Similarly, study of Saxena and D'Souza (2006) showed that adsorption of heavy metal ions to RP was found to follow the order: $Pb^{2+}>Cu^{2+}>Zn^{2+}>Co^{2+}$. Thawornchaisit and Polprasertb (2009) investigated the stabilization of Cd in highly contaminated soils by different phosphate fertilizers, RP decreased the leachable Cd concentrations and the mobile forms of Cd in the contaminated soils as evidence by the TCLP and the sequential extraction tests.

The stabilization efficiency varied depending on types of fertilizers which appears to correlate with dissolution of fertilizer (Zenteno *et al*., 2013). Application of synthetic hydroxyapatite (HA) and natural rock phosphate (RP) in heavy metal (Cd, Cu, Pb, and Zn) contaminated soil effectively reduced the heavy metal water solubility generally by about 84-99% with HA showing slightly superior to RP for immobilizing heavy metals (Mignardi *et al.* 2012). Study of Mignardi *et al*. (2013) on Co and Ni showed that, the application of phosphate amendments to the polluted mine waste soils reduced water-soluble concentrations of Co and Ni by about 99 %, and RP was slightly less effective than HA in immobilizing Co and Ni. However, Cao *et al.* (2009) found that, although RP reduced plant Cu and Zn concentrations in two contaminated soils, the Cu and Zn phytoavailability generally was little affected except for some treatments.

Although the soluble-P treatment has often been shown to immobilize heavy metals effectively in soils, the secondary environmental risk of the use of soluble P as a soil amendment may be unavoidable due to the possibility of P leaching leading to eutrophication (Basta and McGowen 2004; Park *et al.* 2011a; Mignardi *et al.*, 2012; 2013). On this hand, soluble P sources may not be suitable for the remediation of heavy metals, especially in low P-retaining sandy soils (Park *et al.* 2012). Instead of soluble P, less soluble RP can reduce the risk of phosphate-induced eutrophication (Park *et al.* 2012; Mignardi *et al.* (2013).

The possible mechanisms for heavy metal immobilization in the soil involve both surface complexation of the metal ions on the phosphate grains and partial dissolution of the phosphate amendments and precipitation of heavy metal-containing phosphates (Mignardi *et al*., 2012). Based on the possible mechanisms, the surface area and solubility of RP in soil solution determine the efficiency of stabilization. Three procedures can enhance heavy metals immobilization by RP: 1) adding phosphate-solubilizing bacteria (Park *et al.* 2011b), 2) increasing the addition rate and 3) reducing the particle size of RP (Chen *et al*. 2006). Chen *et al*. (2006) suggested that rock phosphate with smaller grain size was more effective to lower the bioavailability and increase the geochemical stability of metals in soil than larger size. The aim of this study is to investigate the effects of RP particles size on immobilizing Pb, Zn, Cu and Cd in lead zinc mine soils by means of a greenhouse experiment. In lead zinc mine, Cd and Cu are usually accompanied contaminants, so our research included the heavy metal Cd and Cu beside Pb and Zn.

2. Materials and Methods

2.1. Soils

The soil used was collected from the Shuikoushan Pb/Zn mine area in Songbai town, Hengyang, Hunan province (China). Surface soil (0-20 cm) was excavated and collected and transported to the laboratory. The soil sample was air-dried, homogenized and sieved to a <2mm with stainless steel mesh prior to use for physical and chemical properties analysis and pot experiment.

Soil pH (soil : water; 1:2.5) was determined by a combination electrode. The properties of the soils were determined according to standard methods recommended by the Chinese Society of Soil Science (Lu, 1999). Total concentrations of metals (Cd, Pb, Zn and Cu) were determined using digestion of soil sample (0.2 g) in 5mL of HNO_3 /$HClO_4$ (3:1) diluted to a volume of 25 ml with distilled water, and measured by inductively coupled plasma spectrometry (ICP-OES, Varian 715 ES, USA). Some basic physiochemical properties and metal contents of the soils are listed in Table 1.

Table 1. Cation exchange capacity (CEC), pH, Organic carbon (OC, %), and heavy metals contents of studied soils.

pH	CEC ($cmol \cdot kg^{-1}$)	OM (%)	Pb ($mg \cdot kg^{-1}$)	Zn ($mg \cdot kg^{-1}$)	Cu ($mg \cdot kg^{-1}$)	Cd ($mg \cdot kg^{-1}$)
4.85	8.08	2.41	881.64	1 065.97	113.08	16.92

2.2. Design

Mineral RP (20% P content) was provided by Yunnan Phosphorization Group Co. Ltd., China. The sample of RP was grind by air-flow disintegrator (QLD, Pinzhen Facility Technology Co. Ltd, Shanghai) and the particle sizes were determined by Centrifugal Sedimentation Particle Size Analyzer (BT-1500, Baitai Co. Ltd). The RP was ground and divided into 4 sizes: D97<101.43 μm (UP), D97<71.12 μm (P1), D97<36.83 μm (P2) and D97< 4.26 μm (P3) (the diameters of 97% of the particles were less than 4.26 μm.), respectively. Every size of the RP was applied at 2.5% and 5%. Soil without RP addition was used as the control (CK). So all together there are 9 treatments: CK, 2.5UP, 2.5P1, 2.5P2, 2.5P3, 5UP, 5P1, 5P2, 5P3. Nutrients were provided by uniform N–K fertilizer application at amounts equal to 100 mg N/K kg^{-1} soil. Each treatment had four replicates. The treated soils were mixed thoroughly and taken into plastic pots (1 kg/pot) and saturated with deionized water. Soil was allowed to equilibrate in the greenhouse for 1 week before sowing the seeds.

Fifty germinated seeds of perennial ryegrass (*Lolium prenne*, L.) were planted in each pot. The pots were randomly arranged in the greenhouse and rearranged several times during the growth period. When the seedlings had grown to about 3 cm, they were thinned to twenty per pot. The seedlings were watered to weight to maintain 100% field capacity of each type of soil every 2 days. The mean growth temperature was 25 ◦C during 14/10h light/dark cycle. The seedlings were harvested after 3 months.

2.3. Plant analysis

After harvest, the seedlings were separated into shoots and roots and rinsed thoroughly with deionized water, and the fresh weights were determined. The samples were then oven dried at 70 ◦C for 48 h, and the dry weight (DW) of shoots and roots was recorded. Dried plant samples were finely ground in a stainless steel miller. Subsamples (0.25 g) of finely ground plant materials were digested in 5 ml high-purity acid HNO_3 at 160 ◦C. The digest was diluted to 25 ml using high purity water, and the concentration of Pb, Zn, Cu and Cd in the digest was determined by inductively coupled plasma mass spectrometry (ICP-OES, Varian 715 ES, USA).

2.4. Statistical analysis

All data of biomass, pH and Heavy metal contents in tissue were subjected to the analysis of variance (ANOVA) with a Duncan test at 95% confidence by SPSS 18.0. Differences at the $p < 0.05$ level were considered to be significant.

3. Results and Discussion

3.1. Plant shoot biomass

Addition of RP increased shoot biomass significantly by 200-816% compared to the control except for 2.5UP ($p<0.05$) (Figure 1), which was in agreement with the reports of Chen *et al*. (2006; 2009) and Mignardi *et al.* (2012). Results of Mignardi *et al*. (2012) showed that, compared to the control, both soluble and insoluble P (RP) treatments significantly increased shoot and root weight of sunflower (Helianthus annuus).Shoot dry weight increased by 31.5%, 32.9%, and 54.1% for RP.

5% level of RP promoted significantly shoot biomass than 2.5% level except for 2.5P3 ($p<0.05$). At the same RP level, the application of smaller particle size resulted in a higher biomass than larger particle size, especially the smallest size P3 (D97< 4.26 μm) ($p<0.01$) (Figure1). The result may be due to two reasons. On the one hand, addition of RP increased the P fertilizer level for plant growth, and on the other hand, addition of RP which immobilize heavy metals in the soil may result in low accumulation of heavy metals in plant reducing their phytotoxicity (Chen *et al*., 2009). The improved growth observed after addition of the smallest size P3 of RP suggested that P3 fraction reduced more effectively phytotoxicity of heavy metals with respect to the other fractions.

3.2. Soil pH

RP addition slightly affected soil pH (Figure 2). Except for 2.5UP, soil pH was increased by different RP rates and particle sizes. At the rate of 2.5%, addition of P1and P2 increased soil pH by around 0.21 and 0.22 units compared to the control ($p<0.05$). The results were in agreement with reports of Tang *et al*. (2004) and Chen *et al*. (2007).Tang *et al*. (2004) added RP at the level of 5000 mg P kg^{-1} to the soil resulted in soil pH increased slightly by around 0.1 unit. Chen *et al*. (2007) reported the soil pH increased due to the addition of RP and HA. This may be due to much $CaCO_3$ contents in RP which makes it as alkaline characteristic (Zhu *et al*., 2004). On the contrary, the application of soluble P amendments such as triple super phosphate (TSP), super phosphate (SSP) and diammonium phosphate (DAP) was reported to decrease soil pH (Chen *et al*., 2007). This effect may induce soil acidic conditions and increase heavy metal solubility. Therefore, the use of less soluble P for immobilization of heavy metals may be more environmentally friendly considering soil condition.

3.3. Heavy metal contents in tissue

Addition of RP reduced Pb contents in both roots and shoots significantly except for 2.5UP treatment ($p<0.01$) (Figure 3 Pb). The concentration of Pb decreased with the decreasing of particle size and increasing application rate. 2.5UP has largest particle size and low application level which may result in non-significant effect compared to the other treatments. Pb contents in shoots reached the lowest level at 5P3 treatment, with a reduction of 54.9% compared to the control. Consistent with the results of previous studies by Chen *et al*. (2009), most of the Pb mainly accumulated to a greater extent in the roots which were 6.6-9.0 folds higher than that in shoots (Figure 3 Pb B/A).

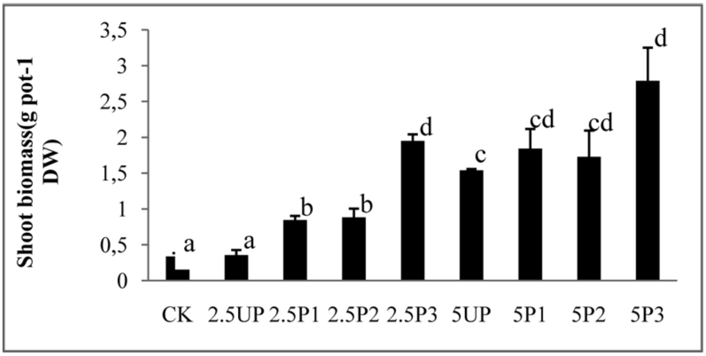

Figure 1. Shoot biomass of ryegrass grown in heavy metal contaminated soils treated with different PR levels and particle sizes. Vertical bars represent standard deviations (n=4).

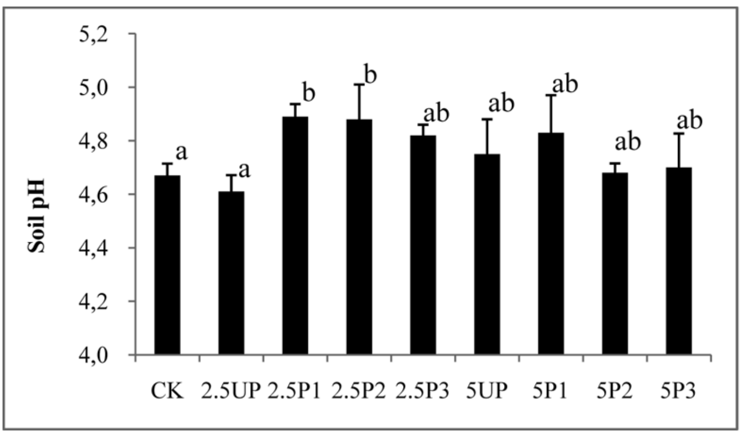

Figure 2. Soil pH with different PR levels and particle sizes treatment. Vertical bars represent standard deviations (n=4).

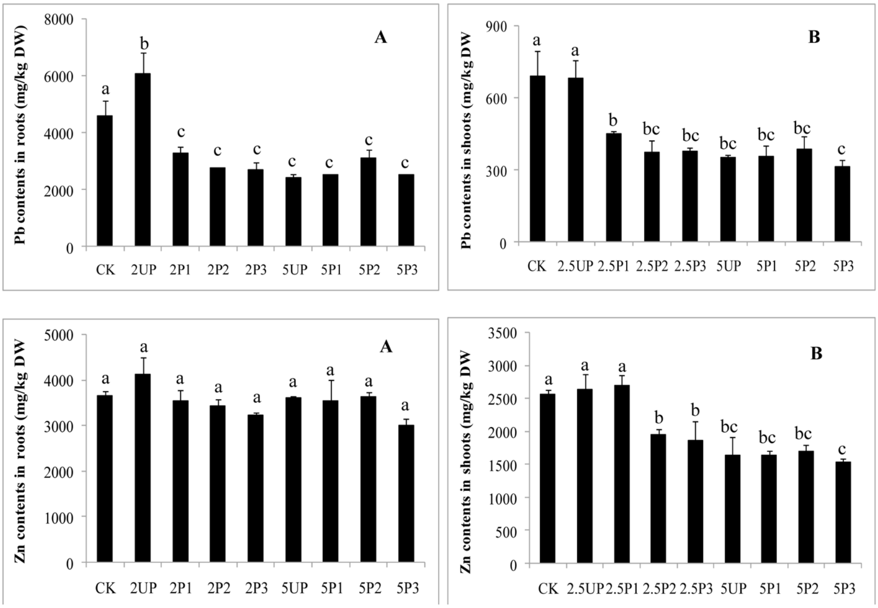

Figure 3a. Heavy metal contents in roots (A) and shoots (B) of ryegrass grown in heavy metals contaminated soils treated with different PR levels and particle sizes. Vertical bars represent standard deviations (n=4).

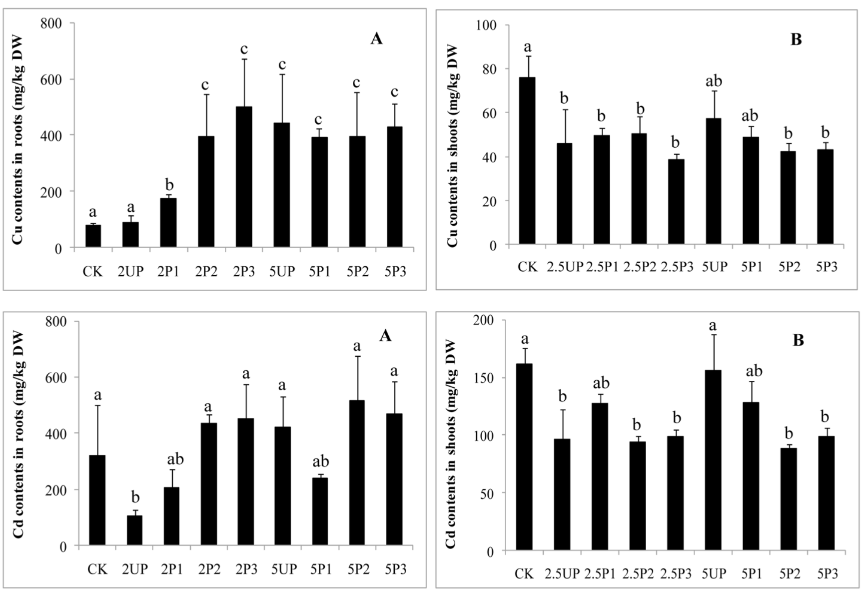

Figure 3b. Heavy metal contents in roots (A) and shoots (B) of ryegrass grown in heavy metals contaminated soils treated with different PR levels and particle sizes. Vertical bars represent standard deviations (n=4).

Zn contents in shoots were reduced significantly by addition of RP except 2.5 UP and 2.5P1, and reached the lowest level at 5P3 which was decreased by 40% (Figure 3 Zn A). However, there's no significant change of Zn contents in roots (Figure 3 Zn B). For Cu, addition of RP reduced the shoot Cu contents significantly compared to the control, and the effects were more remarkable with smaller particle sizes. However, no statistically significant variance between the two RP addition levels has been observed. In the roots, interestingly, addition of RP increased the root Cu contents. The shoot Cd contents in lower particle size (P1 and P2) were decreased significantly, with 45% and 39% decreased at 5P2 and 5P3 treatment respectively. Root Cd contents decreased significantly by addition of RP at some treatments but not showing a regular pattern.

This mineral was shown to be highly stable under a wide range of pH (3-9). Study of Basta and McGowen (2004) showed that, Layered RP at 180 g kg^{-1} showed 99.9% reduction in Pb eluted compared with the untreated check, but was less effective in reduction of eluted Cd (53%) and Zn (24%). While RP mixed with soil at 60 and 180 g kg^{-1} was generally ineffective for reducing Cd, Pb, and Zn elution, with only <27% reduction. RP was also mixed with soil in our experiment treatment and the results at high particle sizes was in consistent with their results for mixed treatment, but the results at lower particle sizes showed more effective than results for high particles and results of theirs even at lower levels, clearly indicating the particle size of RP influence the effectiveness significantly for immobilizing Pb, Zn, Cu and Cd, especially for Pb. This may be due to the lower particle size- induced higher surface area increasing surface complexation of the metal ions on RP grains and partial dissolution of RP and consequently the precipitation of heavy metal-containing phosphates.

4. Conclusions

A green house pot experiment was conducted to study the effects of rock phosphates (RP) with different particle sizes on immobilizing heavy metals in contaminated soils of Pb-Zn mine. Addition of Rock phosphate decreased metal contents in both roots and shoots of *Lolium prenne* L significantly and the particle sizes affect the metal contents significantly. We observed that the treatment of particles less than 4.26 μm at 5% rate was most effective with exception of Zn in roots and Cd in shoots. Our results provided the evidence that, RP can immobilize the Pb, Zn, Cu and Cd in soil and reduce their phytoavailability significantly, and the effects strengthened with the particle size lower and the rate of addition increased, which may be indirect evidence for the mechanisms of PR immobilizing heavy metals.

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