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Field demonstration of reduction of lead availability in soil and cabbage (*Brassica Chinensis* L.) contaminated by mining tailings using phosphorus fertilizers*

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Abstract: A field demonstration of reduction of lead availability in a soil and cabbage (*Brassica Chinensis* L.) contaminated by mining tailings, located in Shaoxing, China was carried out to evaluate the effects of applications of phosphorus fertilizers on Pb fractionation and Pb phytoavailability in the soil. It was found that the addition of all three P fertilizers including single super phosphate (SSP), phosphate rock (PR), and calcium magnesium phosphate (CMP) significantly decreased the percentage of water-soluble and exchangeable (WE) soil Pb and then reduced the uptake of Pb, Cd, and Zn by the cabbage compared to the control (CK). The results showed that the level of 300 g P/m² soil was the most cost-effective application rate of P fertilizers for reducing Pb availability at the first stage of remediation, and that at this P level, the effect of WE fraction of Pb in the soil decreased by three phosphorus fertilizers followed the order: CMP (79%)>SSP (41%)>PR (23%); Effectiveness on the reduction of Pb uptake by cabbage was in the order: CMP (53%)>SSP (41%)>PR (30%). Therefore our field trial demonstrated that it was effective and feasible to reduce Pb availability in soil and cabbage contaminated by mining tailings using P fertilizers in China and PR would be a most cost-effective amendment.

Key words: Lead, Fractionation, Mining tailings, Phosphorus fertilizer, Cabbage, Soil remediation

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INTRODUCTION

Lead (Pb) is toxic to humans, especially young children, and to animals. Lead-contaminated soil is a primary source of Pb exposure to young children. One of the primary sources of Pb contamination is industrial activity including mining and smelting of lead mines, their byproducts mainly mining tailings, leading to Pb accumulation in the soils and risk on human's health through soil ingestion and the food

chain such as vegetables (Wu *et al.*, 2000). Therefore, increasing awareness of the hazard that heavy metals can cause to humans makes it necessary to remediate metal contaminated soils. Some remediation technologies, including thermal, biological, physical/chemical treatments, for lead-contaminated soils have been proposed during the past several decades. Both thermal and biological treatments were not effective in removing heavy metals from contaminated soils. Physical/chemical treatments are often expensive and destructive (Ma *et al.*, 1993). In situ remediation techniques overcome many of these disadvantages. Among the remediation technologies available for contaminated soils, in situ immobiliza-

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tion techniques are of particular interest because they are relatively more cost-effective compared to conventional techniques, such as excavation and off-site disposal (Yang *et al.*, 2001).

Lead phosphates, and in particular pyromorphites, are some of the most stable forms of Pb in soils under a wide range of environmental conditions (Nriagu, 1974; Lindsay, 1979). Based on the low phosphate solubility, a number of studies involving the use of phosphates including P fertilizers for the stabilization of Pb in contaminated soils were carried out (Ma *et al.*, 1995; Cotter-Howells and Capron, 1996; Hettiarachchi *et al.*, 2000; Ryan *et al.*, 2001; Tang *et al.*, 2004). Formation of pyromorphites and significant reduction of Pb bioavailability in the soils upon addition of phosphate rock (PR) or single superphosphate (SSP) was observed in lead-contaminated soils (Ma *et al.*, 1997; Hettiarachchi *et al.*, 2001). Reduced plant uptake of Pb was also observed upon PR or SSP addition to lead-contaminated soils (Hettiarachchi and Pierzynski, 2002; Cao *et al.*, 2002; Chen and Zhu, 2004). Although much knowledge about the mechanisms involved in immobilization of Pb using P amendments is needed, implementation of this technology in the field for remediation of soils and vegetables contaminated by lead and zinc mining tailings is limited, especially in China. Therefore, a field demonstration of this technology, at a site heavily contaminated by heavy metals such as Pb from lead and zinc mining tailings, was undertaken.

The main objective of this field experiment was to evaluate the effectiveness of three kinds of P fertilizers including single superphosphate (SSP),

phosphate rock (PR), and calcium magnesium phosphate (CMP) on in situ Pb immobilization and to observe changes of Pb fractionation in the contaminated soil in relation to uptake and accumulation of Pb by a vegetable plant and to evaluate the feasibility of in situ immobilization of Pb in the contaminated soil using P fertilizers in China.

MATERIALS AND METHODS

Site description

The tested site is located in Shaoxing, Zhejiang Province, China. The studied soil (Typentiaqualf) was heavily contaminated by Pb. The polluted area is about 800 hectares around the abandoned mine. Based on our previous report, level of total Pb range from 5271 to 16369, average of 12552 mg/kg (Xie *et al.*, 2003). The clay mineralogy of the soil was predominantly illitic in nature with kaolin being present in minor amounts. Its selected physical and chemical characteristics are listed in Table 1.

Phosphate fertilizers

The P fertilizers used in this study were single super-phosphate [SSP, a water-soluble P fertilizer, whose main component is $\text{Ca}(\text{H}_2\text{PO}_4)_2$], phosphate rock [PR, a water-insoluble P fertilizer, whose main component is $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$], and calcium magnesium phosphate [CMP, a citric acid soluble P fertilizer, whose main component is $\text{Ca}_3(\text{PO}_4)_2$]. The tested P fertilizers were commonly used in agriculture in China and their main elemental concentrations are given in Table 2.

Table 1 Properties and heavy metal contents of the tested soil

Items	pH	Organic matter (g/kg)	Total Pb (mg/kg)	Total Zn (mg/kg)	Total Cd (mg/kg)	Total Cu (mg/kg)
Tested soil	5.51	21.8	16362	871	5.81	103
Environmental quality standard for soils in China (GB15618-1995)	<6.50		250	200	0.300	50.0
Soil background levels of heavy metals, Zhejiang Province (Wei, 1990)			24.5	84.8	0.202	19.8

Table 2 Concentrations of elements in the tested phosphorus fertilizers

Phosphate fertilizer	pH* (H ₂ O)	Water soluble P (mg/kg)	Citric acid soluble P (mg/kg)	Total P (mg/kg)	Total Pb (mg/kg)	Total Zn (mg/kg)	Total Cd (mg/kg)	Total Cu (mg/kg)
PR	7.41	1.00	24.4	330	240	228	3.40	51.3
CMP	9.51	14.2	52.0	129	3.20	168	1.80	62.8
SSP	3.09	43.0	73.6	152	115	234	1.71	61.0

* Measure in 1:2.5 fertilizer/water suspensions

Vegetable

A Chinese green vegetable (local name: Shanghai Green) *Brassica campestris* L. *chinensis* was selected in this study, as it is not only the most popular vegetable consumed by the local people almost throughout the whole year, but also quite tolerant to heavy metals in the above mentioned contaminated soil. Our preliminary investigation on three main species of local vegetables found that Chrysanthemum (*Dendranthema morifolium* L.) and Spinach (*Spinacia* L.) with greater enrichment coefficients (ratio of metal concentration in plant to metal concentration in soil) of heavy metals could not grow well, while *Brassica campestris* L. *chinensis* with lower enrichment coefficients grew well on the soil (data not shown). Consumption of the vegetable grown around that area would result in possible health risk to the local people. Therefore, scientific evaluation on the effectiveness of P fertilizers is needed.

Experimental plot design

The field plots were established in the highly polluted zone of the site, after the surface soil (0~20 cm depth) was completely homogenized. Each plot was an area of 1.0 m², which were separated by 0.2 m from each other for avoidance of possible inter-plot contamination. P fertilizers including PR, CMP or SSP were applied to the plot at three levels (level 1, 50 g P/m² soil; level 2, 300 g P/m² soil; level 3, 500 g P/m² soil) with 9 treatments. SSP1, SSP2 and SSP3 stand for 50, 300 and 500 g P/m² soil of SSP, the same is for PR and CMP. The amount of P added was calculated on the basis of the total P content of the P fertilizers. Each treatment had 3 replicates. The 30 plots including 9 treatments and 1 control were arranged in a completely randomized design.

The P fertilizers were ground to pass through a 1-mm sieve and then completely mixed with surface soil (0~20 cm depth) in experimental plots. Plots were watered to keep moist until vegetable sowing. After a 6-month equilibrium of added P fertilizers with the soil in treated plots, 1000 seeds of *Brassica campestris* L. *chinensis* were sown in each plot. Urea was applied to each plot 4 weeks after sowing.

Soil and plant sampling

Soil samples (0~20 cm depth) were collected 6 months after P application before sowing. Collected

soils were air-dried and passed through a 1-mm sieve and stored in plastic bottles for further analyses. The edible portion of the vegetable was harvested 8 weeks after sowing and rinsed with deionized water, and then dried in an oven at 65 °C for 3 d. The dried vegetable was ground to pass through a 1 mm sieve for digestion.

Soil Pb fractionation

The procedure of Tessier *et al.* (1979) was used to separate soil Pb into different fractions. The selected procedure was designed to separate total (T) heavy metals in soils into five operationally defined fractions: water soluble and exchangeable (WE), carbonate bound (CB), Fe-Mn oxides bound (FM), organic bound (OC), and residual (RS) fractions. A summary of the procedure is as follows:

Two g of each soil sample was weighed into a 50-ml polycarbonate centrifuge tube and the following fractions obtained:

1. Water soluble and exchangeable (WE): Soil sample was extracted with 16 ml of 1 mol/L MgCl₂ (pH=7.0) for 1 h.

2. Carbonate-bound (CB): The residue from water soluble and exchangeable fraction was extracted with 16 ml of 1 mol/L NaOAc (adjusted to pH 5.0 with HOAc) for 5 h.

3. Fe-Mn oxide-bound (FM): The residue from the carbonate fraction was extracted with 20 ml of 0.04 mol/L NH₂OH·HCl in 25% (V/V) HOAc at 96 °C with occasional agitation for 6 h.

4. Organic-bound (OC): The residue from the Fe-Mn oxide fraction was extracted with 6 ml of 0.02 mol/L HNO₃ and 10 ml of 30% H₂O₂ (adjusted to pH 2 with HNO₃). The mixture was heated to 85 °C for 2 h, with occasional agitation. A second 6 ml aliquot of 30% H₂O₂ (adjusted to pH 2 with HNO₃) was added and the mixture was heated again to 85 °C for 3 h with intermittent agitation. After cooling, 10 ml of 3.2 mol/L NH₄OAc in 20% (V/V) HNO₃ was added and the samples were diluted to 40 ml and agitated continuously for 30 min.

5. Residual (RS): The residues from the organic fraction were digested using a 3:1 HCl:HNO₃ dissolution procedure in a microwave digester (Milestone, Microwave Laboratory Systems).

After each successive extraction, separation was done by centrifuging (Beckman Model J2-21) at

15000 r/min for 30 min. The supernatants were removed with a pipette filtered with 0.2 μm Nucleopore polycarbonate membrane filter, and analyzed for metals. The residue was washed with 8 ml of deionized water followed by vigorous hand shaking, and then followed by 30 min of centrifugation before the next extraction.

Analytical methods

All extractions of treated samples were conducted in triplicate in acid-washed (5% (V/V) HNO_3) polycarbonate labware and filtered through a 0.2 μm membrane (Schleicher & Schuell, Germany). All chemicals used in this study were of analytical grade or better. Double deionized water was used. All edible vegetable samples were digested with concentrated nitric acid in a microwave digester (model: MARS, CEM Corporation, USA) according to modified USAEPA Method 3051 (USAEPA, 1994). The Pb, P, Zn and Cd in vegetable and soil solution were measured by means of an inductively coupled plasma (ICP)-Emission Spectroscopy (model: Perkin Elmer, USA) using high-purity standard solution (EPA, USA) and a standard reference plant material (GBW07602) from the Department of Earth and Mine, was used to verify the accuracy of metal determination. The recovery rates for Pb, P, Zn and Cd were within (90 \pm 10)%. Solution pH was determined by Orion Mode EA 940 pH meter. Other soil properties were measured by conventional methods (Lu, 1999).

Data analysis

All results were expressed as an average of triplicates and treatment effects were determined by analysis of variance using SPSS software (version 10.0, SPSS Inc.). Differences among treatment means were compared by least significant difference (LSD) and Duncan's multiple range tests. For mean separations, LSD values were used at $P < 0.05$.

RESULTS AND DISCUSSION

Effects of application of P fertilizers on soil pH and water-soluble P

Compared with the control, soil pH was significantly affected by the addition of various P fertilizers (Fig.1). At the level of 500 g P/m^2 soil, the

addition of CMP increased soil pH significantly from 5.23 to 7.42; and the addition of PR increased soil pH by around 0.5 units, while the addition of SSP significantly reduced the soil pH by 0.6 units. Both PR and CMP are alkaline materials and hence increased the soil pH values. Monocalcium phosphate (MCP) was the principal P component present in SSP. When SSP was added to the soil, the dissolution of MCP resulted in the formation of slowly soluble dicalcium phosphate (DCP) with a release of phosphoric acid close to the fertilizer granules, the phosphoric acid subsequently dissociated into P ions and acidic hydrogen ions, leading to a substantial decrease in soil pH in SSP treated plots (Bolan *et al.*, 2003):

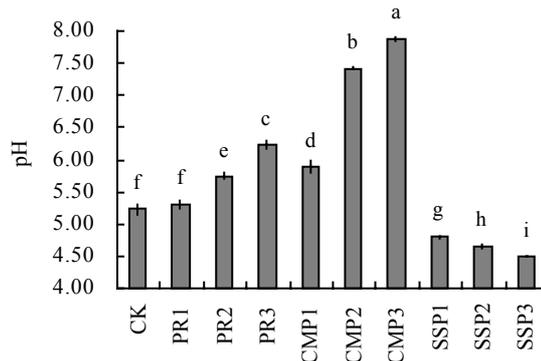
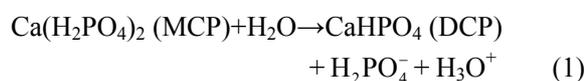


Fig.1 Effects on soil pH caused by the addition of three P fertilizers

SSP1, SSP2 and SSP3 stand for level 1 (50 g P/m^2 soil), level 2 (300 g P/m^2 soil) and level 3 (500 g P/m^2 soil) of SSP. The same is for PR and CMP. CK: Control. Means with the same letter are not significantly at $P < 0.05$

Water-soluble P concentration of soil samples is displayed in Fig.2. It was apparent that the addition of all three P fertilizers increased water-soluble P concentration of the soil. At the level of 500 g P/m^2 soil, the addition of SSP increased to the greatest extent water-soluble P concentration in soil, and followed by CMP. However, water-soluble P concentrations in the PR-treated soil were not significantly different from those in the CK soil. This was not surprising, because PR is a water-insoluble (slow-release) fertilizer, while SSP or CMP are water-soluble (fast release) fertilizers (Bolan *et al.*, 2003). This is also proved by the data of soluble P in Table 2.

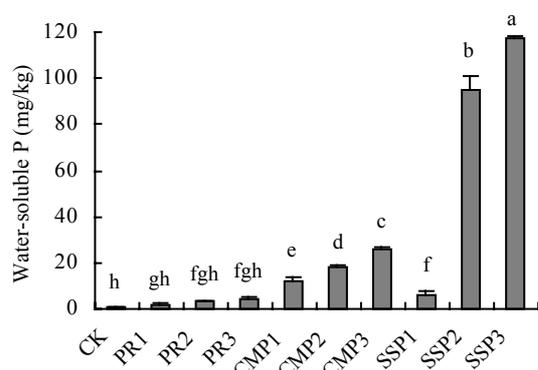


Fig.2 Effects of application of P fertilizers on water-soluble P in the soil

CK, PR1, PR2, PR3, CMP1, CMP2, CMP3, SSP1, SSP2 and SSP3 are the same as in Fig.1. Means with the same letter are not significantly at $P < 0.05$

Effects of application of P fertilizers on Pb fractionation

The sequential extraction procedure proposed by Tessier *et al.* (1979) was conducted to investigate the change of Pb fractionation in soil after application of P fertilizers. Without P fertilizers treatment, lead in the contaminated soil was primarily associated with the RS fraction (38.1%) and OC fraction (30.5%). Although the proportion of Pb associated with WE was not so large (3.82%), its actual concentration (667 mg/kg) was very much more than the normal range in the natural soils. It is well known that the WE fraction is the most bioavailable and phytoavailable among all 5 fractions (Xian, 1989; Bolan *et al.*, 2003). Thus, lead in WE fraction in the studied soil was easily mobile and could pose a potential threat to the eco-environment. Data showed that application of P fertilizers to the soil significantly reduced extractable Pb in the nonresidual fraction while it increased Pb concentration in the residual fraction (Fig.3). The percentage of Pb reduction in the nonresidual fraction ranged from 20.7%~39.4% after application of P fertilizers, and it was mainly due to reduction of Pb in the OC fraction, which accounts for 54% to 71% of the total reduction of the nonresidual fraction in the soil (Fig.3). It was possible that some of the Pb transformation from the nonresidual fraction to residual fraction could have occurred during the extraction process (Ryan *et al.*, 2001). However, the phenomenon that Pb in WE fraction significantly reduced (by 21.9%~81.4%) after P application strongly demonstrated that the effectiveness of P

fertilizers on reducing Pb availability in the contaminated soil was notably obvious in the field. Some researchers reported that the great increment of RS Pb in the soil after P amendment was due to the formation of pyromorphite-like mineral (Ma *et al.*, 1997; Ricardo *et al.*, 2003). Therefore, our results suggested that the mechanism of Pb reduction in the nonresidual fractions after application of P fertilizers was through formation of pyromorphite-like mineral.

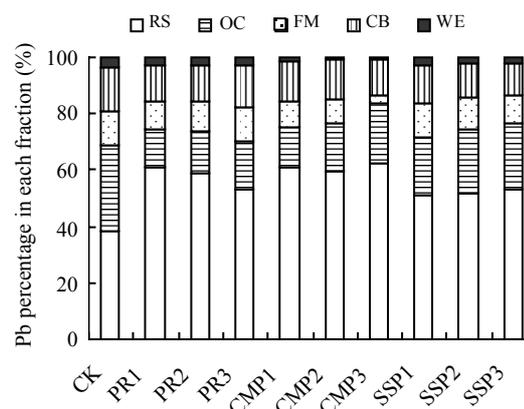


Fig.3 Effects of addition of P fertilizers on Pb fractionation

WE: Water soluble and exchangeable; CB: Carbonate bound; FM: Fe-Mn oxides bound; OC: Organic bound; RS: Residual. CK, PR1, PR2, PR3, CMP1, CMP2, CMP3, SSP1, SSP2 and SSP3 are the same as in Fig.1

Increasing the application rate of P fertilizers significantly reduced WE fraction slightly increased RS fraction Pb (Fig.3). Statistical analysis indicated that there was significant reduction in WE Pb concentration when the application rate of P to the soil increased from 50 g P/m² soil to 300 g P/m² soil, while there was no remarkable reduction of WE Pb concentration from 300 g P/m² soil to 500 g P/m² soil. It was possible that phosphorus concentration in the soil solution may efficiently precipitate WE fraction soil Pb to form Pb phosphates at the level of 300 g P/m² soil. As a result, there was no significant effect in the reduction of soil Pb availability by increasing the application rate of P fertilizers after the level of 300 g P/m² soil is exceeded. It was also suggested that the level of 300 g P/m² soil was the most cost-effective application rate of P fertilizers for reducing Pb availability at the first stage of remediation. At the level of 300 g P/m² soil, the effect of residual

fraction Pb increased by P fertilizers was in the order: CMP (55%), PR (54%)>SSP (37%). Effects of P fertilizers on reduction of WE fraction of Pb in the soil was in the order: CMP (79%)>SSP (41%)>PR (23%). PR was more effective in converting Pb from nonresidual to residual fraction because Pb could be directly adsorbed on the nondissolved fraction of PR and formation of pyromorphite-like mineral (mainly fluoropyromorphite-like mineral). Similarly, Cao *et al.* (2002) also reported that PR was more effective than SSP in reducing Pb bioavailability in the Pb contaminated soil in their experiment. Among all three P fertilizers, CMP was most effective in decreasing WE fraction and increasing residual fraction of Pb, partly due to increased soil pH from 5.7 to 6.5~7.8 after application of CMP leading to Pb precipitation from WE. On the other hand, PR is a water-insoluble (slow-release) fertilizer (Bolan *et al.*, 2003), which cannot supply as much soluble phosphorus for reducing WE Pb bioavailability in the soil as CMP and SSP do. Therefore it was concluded that the effect of all three P fertilizers on WE fraction of Pb in the soil followed the order: CMP>SSP>PR.

Effects of P fertilizers application on Pb uptake by cabbage

Pb concentrations in shoot tissue of cabbage grown in the treated soil plots are listed in the Table 3. Compared with the control, the addition of PR, CMP or SSP significantly ($P<0.05$) decreased the Pb concentration in the cabbage by 16%~35%, 47%~58%, and 32%~50%, respectively. Similar results were obtained in previous investigation in which Pb concentration in the tissue of *St. Augustine grass*

(*Stenotaphrum secundatum*) was reduced after application of P to Pb polluted soils, probably because of the formation of Pb-P precipitate on the root surface in the root rhizosphere and in the bulk soil (Cao *et al.*, 2002). Therefore, we suggest that the formation of pyromorphite-like mineral (mainly fluoropyromorphite-like mineral) in the soils and on the root cell wall of cabbage could be responsible for decreasing Pb translocation from the roots to shoots, thereby reducing Pb concentration in shoot.

Pb uptake by plants is related to soil Pb phytoavailability, and different chemical forms of Pb have different availability (Cao *et al.*, 2002). A step regression analysis was carried out between Pb concentrations in the cabbage and five Pb fractions (WE, CB, FM, OC, RS) in the soil. The result indicated that WE fraction of Pb in the soil was most closely correlated with Pb contents in the cabbage, with an equation as $Y=3.771+0.01271X_1$, $R=0.901$ ($P<0.05$), where X_1 , Y stands each for WE fraction soil Pb and cabbage Pb uptake. Similar results were also reported (Xian, 1989; Chen and Zhu, 2004). Furthermore, there was no significant reduction in Pb concentration in the cabbage because there was no significant reduction in WE fraction of Pb in the soil when increasing application rate of P to the soil from 300 g P/m² soil to 500 g P/m² soil. It was demonstrated that the reduction of Pb concentration in vegetable primarily resulted from decreased Pb phytoavailability via reduction of WE (the most phytoavailable fraction) Pb after application of P fertilizers, consequently leading to decreased Pb availability in the soil.

At the level of 300 g P/m² soil, there was no remarkable difference between SSP and PR in the

Table 3 Effects of P fertilizers on uptake of Pb, Zn and Cd by cabbage (*Brassica Chinensis* L.)

Treatments	Pb (mg/kg)	Zn (mg/kg)	Cd (mg/kg)
CK [#]	13.54±0.04 a*	23.65±1.75 a	1.075±0.295 a
PR1	11.40±0.05 b	21.80±0.11 ab	0.825±0.018 bc
PR2	9.65±1.14 c	16.13±0.60 c	0.635±0.016 cde
PR3	8.81±0.80 c	14.37±0.62 c	0.542±0.002 def
CMP1	7.22±0.24 de	11.62±0.11 d	0.422±0.038 ef
CMP2	6.30±0.22 ef	8.35±0.26 e	0.364±0.044 f
CMP3	5.71±1.16 f	6.34±0.61 e	0.356±0.032 f
SSP1	9.24±0.40 dc	20.97±0.64 b	0.898±0.006 ab
SSP2	7.63±0.45 cd	23.37±2.03 a	0.816±0.059 bc
SSP3	6.77±0.14 ef	20.77±2.39 b	0.681±0.003 bcd

[#]: CK, PR1, PR2, PR3, CMP1, CMP2, CMP3, SSP1, SSP2 and SSP3 are the same as in Fig.1; *: Means with the same letter in the same column are not significantly at $P<0.05$

reduction of cabbage Pb uptake, while both were markedly smaller than CMP (Table 3). It was possible that added CMP underwent sufficient dissolution to immobilize Pb via precipitation of pyromorphite-like mineral, and also increased soil pH and then induced Pb phosphate precipitation, because CMP is alkaline citric-acid-soluble fertilizer.

Effects on of P fertilizers application on Cd and Zn uptake by cabbage

Data on Cd and Zn concentrations in shoot of cabbage grown in the treated soil plots are listed in Table 3. Cadmium concentrations in shoot ranged from 0.356 to 0.898 mg/kg, and generally decreased significantly after application of CMP, PR or SSP at all three P levels except for SSP addition at level of 50 g P/m² soil probably because the lowest pH and lower P level indicate that Cd uptake was influenced by the addition of phosphorus fertilizers. The addition of P may reduce Cd phytoavailability through a combination of several mechanisms, such as sorption (including phosphate-induced Cd adsorption and surface complexation), precipitation, or co-precipitation (Laperche and Traina, 1998; Valsami-Jones *et al.*, 1998). No new Cd phosphate minerals identified by XRD (X-radiation diffraction) were formed by the end of the experiment. Therefore, it was speculated that a solid residue containing Cd was Ca-Cd phosphate or Ca-Pb-Cd phosphate (Valsami-Jones *et al.*, 1998). Chen *et al.* (1997) suggested that reduction in aqueous Cd concentrations in solutions with apatite addition occurred primarily because of sorption mechanisms, such as surface complexation, and ion exchange rather than precipitation of Cd phosphate.

Zn concentrations in the aboveground biomass of cabbage ranged from 6.34 to 23.37 mg/kg, and decreased significantly to below permitted limit of zinc in foods (Chief Newsroom of China Standard Press, 1993) after application of P fertilizers at all three P levels, with the exception of SSP which may be due to its lower pH. Hettiarachchi and Pierzynski (2002) reported that plant tissue concentrations of Pb, Zn and Cd were consistently reduced in the presence of soluble P, possibly through the formation of mixed-metal phosphates. Similarly, addition of CMP and SSP decreased Zn concentration in the cabbage aboveground biomass may possibly be due to formation of mixed-metal phosphates (such as Zn-Pb-Cd

phosphate). They also reported that the addition of PR reduced plant tissue Zn concentrations possibly through enhanced sorption mechanisms such as surface complexation, and ion exchange. Cao *et al.* (2004) reported that Zn immobilization by PR was mainly attributable to the surface adsorption or complexation in the soil system.

Trend of Cd and Zn concentrations change in the aboveground biomass of cabbage is attributable to increased P level similar to that of Pb concentrations change in soil. At the level of 300 g P/m² soil, effects of three P fertilizers on Cd and Zn concentrations in cabbage: CMP>PR>SSP. It was possible that added CMP not only underwent sufficient dissolution to immobilize Pb via precipitation of mixed-metal phosphates (such as Zn-Pb-Cd phosphate) mineral, but also increased soil pH and then induced Cd or Zn phosphate precipitation, because CMP is an alkaline citric-acid-soluble fertilizer. Like CMP, addition of PR could also increase soil pH and then induce Cd or Zn phosphate precipitation, and immobilized Cd and Zn via surface adsorption or complexation at the same time.

CONCLUSION

This study indicated that the addition of all three P fertilizers significantly reduced water soluble and exchangeable soil Pb due to a significant increase in residual soil Pb compared with the control, leading to reduced uptake of Pb, Cd and Zn by cabbage (*Brassica Chinensis* L.). It was suggested that P fertilizers are effective and feasible for in situ immobilization of Pb in soils contaminated by lead/zinc mining tailings in China. The application rate of phosphorus fertilizers at level of 300 g P/m² soil, was enough to reduce Pb availability in the soil at the first stage of remediation, and at this P level, the effect of phosphorus fertilizers on increased residual fraction of Pb in the soil was: CMP, PR>SSP; the effect of all three P fertilizers on WE fraction of Pb in the soil was: CMP>SSP>PR. Compared with the control, the addition of PR, CMP or SSP significantly ($P<0.05$) decreased the Pb concentration in cabbage by 16%~35%, 47%~58%, and 32%~50%, respectively. Result from step regression analysis indicated that WE fraction of Pb in the soil was very closely corre-

lated with Pb contents in plant. Above all, it is concluded that PR is a very cost-effective amendment for Pb immobilization considering both its effectiveness and price, and advantage of least impact on soil pH and the lowest risk of eutrophication to the environment.

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