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Reversed Effects of Phosphate Fertilizer on Reducing Phytoavailability of Cadmium in Mine Tailing Affected Soil

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ABSTRACT: To reduce effectively cadmium (Cd) phytoavailability by phosphate in mine tailing affected soil, fused and super phosphate (FSP), a main phosphate fertilizer in South Korea, was selected as phosphate source and then applied at the rates of 0, 78, 390, and 780 P_2O_5 kg ha^{-1}. FSP did not decrease Cd extractability and radish Cd uptake, but increased significantly. The effect of Cd supplement and soil negativity increase through FSP application was not significant. Soil pH decreased markedly with increasing FSP application, which increased significantly soil Cd extractability and radish Cd uptake. As a result, phosphate fertilizer for reducing Cd phtyoavailability in heavy metals contaminated soil should be carefully selected as alkaline type.

Key Words: Cadmium, phosphate, fused and super phosphate, radish

INTRODUCTION

In Korea, over 1000 metalliferous mines were distributed along mineralized zones; most of the mines were abandoned due to a lack of ore minerals in the early 1980s. However, large amounts of mine wastes including tailings have been left without proper environmental treatment. The abandoned mines became an important point source of toxic elements including As, Cd, Cu, Pb and Zn in the surface environment.

In the national wide survey in 1995-1997, 7.2% of 314.9 ha arable soil nearby mining area was found to be contaminated by heavy metals[1)]. Specially, *Bongsan* gold mining area (128°01′N and 34°37′E) in *Hapcheon, Gyeongnam* province, *South Korea,* is famous for Cd contained area. Average 0.1 N HCl extractable Cd concentration of paddy soils was 2.18-3.00 mg kg^{-1}. According to the Korean Soil Environmental Conservation Act, soils containing over 1.5 and 4.0 mg kg^{-1} of Cd extracted by 0.1 N HCl solution need to be continuously monitored and not used for agricultural purposes such as crop planting, respectively. Even though rice cultivation has prohibited in this area since 2003, farmers have cultivated rice and confronted with the local government.

The mobilization of metals in soils for plant uptake and leaching to groundwater can, however, be minimized by reducing their bioavailability through chemical and biological immobilization[2)]. Recently there has been keen interest in the immobilization of heavy metals using a range of inorganic compounds, such as lime, phosphate fertilizers and alkaline biosolid[3)]. These compounds are found to be highly effective in reducing the bioavailability of metals in soils.

In the field trials, we examined the potential value of phosphate fertilizers on the immobilization and the subsequent reduction in the phytoavailability of Cd in a mine tailing affected soil. However, fused super

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phosphate (FSP), a main phosphate fertilizer in Korea, did not reduce Cd phytoavailability but increased contrarily from our expectation. In this paper, we analyzed the reason why FSP increased Cd phytoavailability in soil.

MATERIALS AND METHODS

Select the target site and field test

To investigate the effect of phosphate fertilizer on the plant uptake of Cd, a mine tailing affected upland soil was collected from an abandoned Bongsan gold mine area (128°01′N and 34°37′E) in *Bongsan-myeon Hapcheon-gun Gyeongnam* province, air-dried, meshed within 4 mm of particle size and packed in macro pot for plant growth test in August 2004. Characteristics of the soils used for the field test are described in Table 1. Before the test, heavy metals extracted using 0.1 N HCl solution and Cd fraction fractionated by the sequential extraction procedure are described in Table 2 and 3, respectively. Cd concentration extracted by 0.1N HCl solution was mean 6.1 mg kg^{-1} which exceeded extremely the countermeasure criteria (4.0 mg kg^{-1}) of the Korean Soil Environmental Conservation Act, but other heavy metals were less than the criteria. Cd was detected negligibly in water soluble and acidic phase having ca. 10% of total concentration and distributed mainly with immobile and less bioavailable types. Macro pot size was L. 5 m × W. 2 m × D. 0.5 m, and four treatments of fused and super phosphate (FSP) were selected with the rates of 0, 78, 390 and 780 kg P_2O_5 ha^{-1}. Compost (30 Mg ha^{-1}) and chemical fertilizers N (180 kg ha^{-1}), K_2O (160 kg ha^{-1}) and $Ca(OH)_2$ (2 Mg ha^{-1}) were applied in all the treatments with the same level. A radish cultivar (*Raphanus sativa* L.) was seeded at intervals of 20 cm × 15 cm by hand in the experimental field on September 1, 2004 and harvested on November 1, 2004.

Chemical analysis

Soil samples were collected from the surface layer (15 cm depth) before and after the experiment and air-dried for chemical analysis. The chemical properties of the sieved soils (<2 mm) were analyzed by different standard methods such as pH (1:5 water extraction), organic matter content[4], and levels of exchangeable Ca^{2+}, Mg^{2+}, Na^+ and K^+ (1 M NH_4-acetate pH 7.0, AA, Shimazu 660). The available P_2O_5 content was determined using the Lancaster method[5]. The surface charge was

Table 1. Physical and chemical properties of the soils used for this study

Item	pH (H_2O, 1:5)	OM (g kg^{-1})	T-N (g kg^{-1})	Av.P_2O_5 (mg kg^{-1})	CEC (cmol+ kg^{-1})	Ex. Cation ($cmol^+$ kg^{-1})			
						K	Ca	Mg	Na
Mean	5.99	49.7	1.40	156	8.58	0.32	3.48	0.60	0.08
SD*	0.00	0.75	0.00	1.68	0.32	0.03	0.14	0.03	0.00

Note) * SD means standard deviation.

Table 2. Contents of 0.1N HCl extractable heavy metals in soil used for this study

Heavy metals	Cd	Cu	Mn	Pb	Zn
	mg kg^{-1}				
Mean	5.11	11.53	41.28	7.00	53.24
SD	0.10	0.50	2.29	0.24	0.90

Note) 0.1 N HCl extractable As, Cr and Ni were not detected, and SD means standard deviation.

Table 3. Characteristics of cadmium fraction in soil used for this study

Cadmium Fraction	Water soluble	Acidic	Reducible	Oxidizable	Residual	Total
	mg kg^{-1}					
Mean	<0.01	0.71	1.79	2.95	0.57	6.03
SD	-	0.02	0.05	0.12	0.31	0.13

Note) * SD means standard deviation.

measured using 0.1 M NaCl following the ion retention method. Heavy metals in soils were extracted using 0.1 N HCl. Exchangeable Cd in soil was extracted using 1 M NH_4-acetate pH 7.0. Cd of heavy metals was fractionated by the sequential extraction procedure of Tessier et al.[6] in triplicate. Extractions were conducted in 50 ml polypropylene centrifuge tubes. Between each successive extraction, the supernatant was centrifuged at 6000 rpm for 15 min, and filtered.

The radish plants were separated into stem and root parts, oven-dried at 70℃ for 72 h., ground and then digested using a ternary solution (HNO_3:H_2SO_4:$HClO_4$,10:1:4 volume/volume) for determining Cd. Heavy metals were quantified using ICP-AES (Inductively Coupled Plasma Absorption Emission Spectrophotometer, GBC model X-100, Australia).

RESULTS AND DISCUSSION

Radish yield was increased slightly with increasing FSP application. It was maximized at level of FSP 390 kg P_2O_5 ha^{-1} (Fig. 1).

Different with our expectation, FSP selected in this study showed adverse effect on reducing Cd extractability and phytoavailability (Fig. 2 and Table 4). Cd concentration in radish roots and shoot parts increased significantly with increasing FSP fertilizer application. For example, Cd concentration was ca. 3.1 mg kg^{-1} of shoot part in the control and increased to maximum ca. 7.5 mg kg^{-1} in 780 kg P_2O_5 ha^{-1} of FSP fertilizer application, which applied 10 times higher than the recommendation level of phosphate to radish[7]. Cd concentration was ca. 5 times higher in radish shoot than root part, a main edible part. However, Cd toxicity was not observed during radish cultivation in this study. Exchangeable Cd concentration in soil collected at radish harvesting time increased significantly with increasing FSP application. For example, it was 0.87 mg kg^{-1} in the control and increased to maximum 1.29 mg kg^{-1} in 780 kg P_2O_5 ha^{-1}.

In general, Cd extractability and phytoavailability is decreased with phosphate application. Several reasons could be attributed to phosphate-induced immobilization of Cd in soils: (i) increase in pH, (ii) increase in surface charge, (iii) co-adsorption of phosphate and Cd as an ion pair, and (iv) surface complex formation of Cd on the phosphate compound. Specific adsorption of anions such as phosphate and organic acids increase the net negative charge of variable charge surfaces[8-10]. Increasing phosphate addition caused a significant increase in Cd^{2+} adsorption by soils dominated with variable charge components[11-12]. This has been attri-

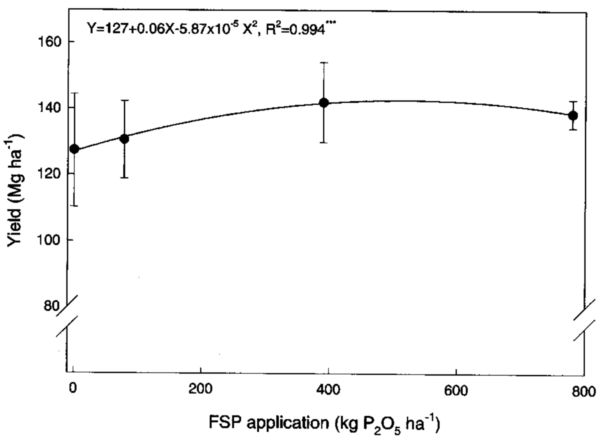

Fig. 1. Fresh yield response of radish cultivated at different levels of fused and super phosphate fertilizer (FSP) application.

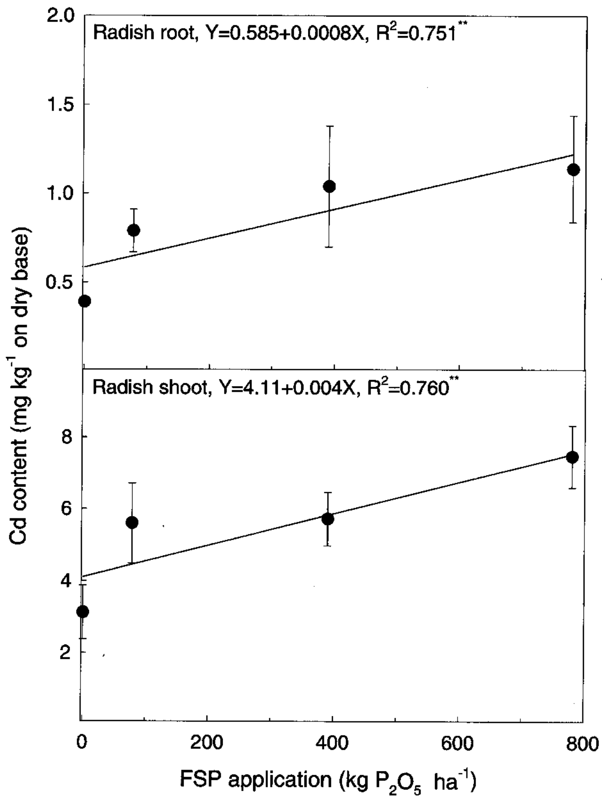

Fig. 2. Cd uptake characteristics of radish shoot and root cultivated at different levels of fused and super phosphate fertilizer (FSP) application.

Table 4. Chemical properties of soil after radish harvesting

FSP application (kg P_2O_5 ha^{-1})	pH (H_2O, 1:5)	OM (g kg^{-1})	T-N (g kg^{-1})	Av. P_2O_5 (mg kg^{-1})	Ex. Cation ($cmol^+$ kg^{-1})				Ex. Cd (mg kg^{-1})	Negativity ($cmol^+$ kg^{-1})
					K	Ca	Mg	Na		
0	7.29	35.2	1.3	191	0.44	4.71	1.50	0.09	0.87	9.33
78	7.28	41.4	1.5	259	0.43	5.13	1.59	0.09	1.13	8.91
390	6.82	39.3	1.3	334	0.34	4.49	1.38	0.07	1.29	8.11
780	6.76	39.3	1.4	591	0.27	4.84	1.59	0.07	1.29	9.01

Note) FSP means fused and super phosphate fertilizer.

buted to increases in surface negative charge after phosphate adsorption.

Among the factors which can increase Cd uptake of radish, Cd supplement effect through FSP fertilizer can be ignorable in this study, since average Cd concentration of FSP is less than 1.8 mg kg^{-1} [13]. In general, Cd concentration in the plant tissue decreased with increasing pH except for high pH value. However, soil pH decreased significantly with increasing FSP application (Table 4) and this pH decrease might be a main reason to increase radish Cd uptake. Soil pH was 7.29 in the control and then decreased to 6.76 with 780 kg P_2O_5 ha^{-1} of FSP application. Phosphate-induced variation in soil pH influenced the solubility of Cd in soils. The effect of phosphate addition on soil pH depends on the buffering capacity of the soil, the nature of phosphate and the extent of phosphate adsorption[14]. While the addition of nitrogen- and calcium-containing phosphate fertilizers generally decreases soil pH due to acidification reactions, addition of other phosphate fertilizers increases soil pH mainly due to the ligand-exchange (i.e., OH.ions) phosphate adsorption reaction. FSP is made of fused phosphate ($Mg_3CaP_2O_9 \cdot 3CaSiO_2$) and calcium phosphate ($Ca(H_2PO_4)_2 \cdot H_2O$)[15], and its pH is around 5. With increasing this acidic phosphate fertilizer application, soil pH decreased significantly and then increased Cd extractability and phytoavailability.

A constant tendency of soil negativity, as indicated by Na^+ adsorption, was not found in FSP applied soil (Table 4). As FSP application increased, soil negativity decreased by ca. 390 kg P_2O_5 ha^{-1} and, thereafter, increased. The effect of phosphate adsorption on increasing soil negativity might be slight on the low FSP fertilizing condition less than 390 kg P_2O_5 ha^{-1} in this study and significant at the high FSP fertilization more than 780 kg P_2O_5 ha^{-1}. As a result, the increase of soil negativity by phosphate application in this test scarcely affected on decreasing Cd extractability and phytoavailability.

CONCLUSION

Fused and super phosphate fertilizer (FSP), a main phosphate fertilizer in Korea, was selected for reducing crop plant Cd uptake. It was found that Cd extractability and radish Cd uptake was not decreased but increased significantly. The effect of Cd supplement and soil negativity increase through FSP application were ignorable. Soil pH decreased markedly with increasing FSP application, which increased significantly soil Cd extractability and radish Cd uptake. In conclusion, phosphate fertilizer for reducing Cd phytoavailability in heavy metal contaminated soil should be carefully selected.

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REFERENCES

1. National Institute of Agricultural Science and Technology (NIAST) (1997) Survey of heavy metals contamination degree of arable soil located in mining area. Annual Report (Department of Agricultural Environment). pp. 237-243. (*in Korean*).
2. Adriano, D. C. (2001) Trace Elements in Terrestrial Environments; Biogeochemistry, Bioavailability and Risks of Metals. 2nd edn. Springer, New York.

pp. 866.
3. Basta, N. T., Gradwohl, R., Snethen, K. L., and Schroder, J. L. (2001) Chemical immobilisation of lead, zinc and cadmium in smelter contaminated soils using biosolids and rock phosphate. J. Environ. Qual. 30: 1222-1230.
4. Allison, L. E. (1965): Organic carbon. In Methods of Soil Analysis. Part II, Ed. C.A. Black, Am. Soc. Agron. Inc. Publ., Madison, WI. p. 1367-1376.
5. RDA (Rural Development Administration, Korea) (1988) Methods of Soil Chemical Analysis. National Institute of Agricultural Science and Technology, RDA. Suwon (*in Korean*).
6. Tessier, A., Campbell, P. G. C., and Bisson, M., (1979) Sequential extraction procedure for the speciation of particulate trace metals. Analytical chemistry 51; 7. 844-851.
7. RDA (Rural Development Administration, Korea), (1999). Recommendation standard of fertilization for crops. National Institute of Agricultural Science and Technology, RDA. Suwon (*in Korean*).
8. Bolland, M. D. A., Posner, A. M., and Quirk, J. P. (1977) Zinc adsorption by goethite in the absence and presence of phosphate. Aust. J. Soil Res. 15, 279-286.
9. Kuo, S. (1986) Concurrent adsorption of phosphate and zinc, cadmium, or calcium by a hydrous ferric oxide. Soil Sci. Soc. Am. J. 50: 1412-1419.
10. Naidu, R., Kookana, R.5., Sumner, M. E., Harter, R. D., and the late Tiller, K. G. (1996) Cadmium adsorption and transport in variable charge soils: A review. J. Environ. Qual. 26: 602-617.
11. Naidu, R., Bolan, N. S., Kookana, R. S., and Tiller, K. G. (1994) Ionic strength and pH effects on the adsorption of cadmium and the surface charge of soils. Eur. J. Soil Sci. 45: 419-429.
12. Bolan, N. S., Naidu, R., Khan, M. A. R., Tillman, R. W., and Syers, J. K. (1999) The effects of anion sorption on sorption and leaching of cadmium. Aust. J. Soil Res. 37: 445-460.
13. RDA (Rural Development Administration, Korea) (2001) Korean Fertilizer Management Act. Suwon. (*in Korean*).
14. Havlin, J. L., Tisdale, S. L., Nelson, W. L., and Beaton, J. D. (1999) Soil Fertility and Fertilizers: An Introduction to Nutrient Management. 6th ed. Prentice Hall, NJ. pp. 499.
15. Cho, S.J. (1990) Shingo Fertilizer Science. Hyangmoon-sa, Seoul. pp. 218-239 (*in Korean*).