Available online at www.sciencedirect.com

ScienceDirect

Chemosphere 70 (2008) 2009–2015

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Feasibility of phosphate fertilizer to immobilize cadmium in a field

Chang Oh Hong [a], Do Kyoung Lee [b], Pil Joo Kim [a,c,*]

[a] *Division of Applied Life Science (BK21), Graduate School, Gyeongsang National University, 900, Kaswa-dong, Jinju 660-701, South Korea*
[b] *Plant Science Department, South Dakota State University, Brookings, SD 57007, USA*
[c] *Institute of Agriculture and Life Sciences, Gyeongsang National University, 900, Kaswa-dong, Jinju 660-701, South Korea*

Received 22 May 2007; received in revised form 13 September 2007; accepted 13 September 2007
Available online 30 October 2007

Abstract

To reduce effectively cadmium (Cd) phytoextractability by phosphate fertilizer in Cd contaminated soil, fused and superphosphate (FSP) was applied at the rate of 0, 33.5 (recommendation level), 167.5, and 335 kg P ha^{-1} for radish (*Raphanus sativa* L.). Unlike from what we expected, soil Cd extractability and Cd concentration in radish increased with increasing FSP application in the field. To determine the effect of FSP on Cd immobilization, FSP was mixed with the selected soil at the rate of 0, 200, 400, 800, and 1600 mg P kg^{-1} and then incubated for 8 weeks. As observed in the field study, NH_4OAc extractable Cd concentration increased slightly with FSP addition up to 400 mg P kg^{-1} and thereafter dramatically decreased upon increasing its application rate. Soil pH and negative charge were decreased at low level of FSP application up to 400 mg P kg^{-1}, but thereafter continually increased with increasing application level. This could be indirect evidence that net soil negative charge was increased by the specific adsorption of phosphate at the high rate of FSP application over 400 mg P kg^{-1}. The labile Cd fraction (water soluble and exchangeable + acidic fraction) increased with increasing FSP application by 400 mg P kg^{-1} and thereafter gradually decreased with corresponding increase in unlabile fraction (oxidizable and residual fraction). Based on these results, FSP might be applied with a very high rate over 800 mg P kg^{-1} to decrease Cd extractability in the selected field. However, this level is equivalent to 1440 kg P ha^{-1}, which is about 43 times higher than the recommendation levels for radish production and resulted in a significant increase in water soluble P concentration creating a new environmental problem. Therefore, the feasibility of FSP to reduce Cd extractability in the field is very low.

Keywords: Cadmium; Phosphate; Immobilization; Radish; Fused and superphosphate

1. Introduction

Cadmium (Cd), which is both readily available and highly toxic, has been identified as the most common heavy metal reaching the food chain through plant transfer. According to the Korean Soil Environmental Conservation Act, soils containing over 1.5 mg kg^{-1} of Cd extracted by 0.1 N HCl solution need continuous monitoring and soils containing over 4.0 mg kg^{-1} of Cd extracted by 0.1 N HCl solution should not be used for agricultural purposes such as crop production (ME, 2005). For example, an abandoned *Bongsan* gold mining area in the southeast part of Korea (128°01′N and 34°37′E) caught the severe attention by mass media due to Cd contamination. Mean 0.1 N HCl extractable Cd concentration of paddy soils located on the downstream of the mining area ranged 2.18–3.00 mg kg^{-1}. In 2002, Cd concentration in rice (*Oryza sativa* L.) harvested in this area was 0.425–0.610 mg kg^{-1} Cd, which exceeded the criteria (0.2 mg kg^{-1}) for food safety.

The mobilization of metals in soils for plant uptake and leaching to groundwater can be minimized by reducing their bioavailability and activity in soil solution through chemical and biological immobilization (Adriano, 2001).

* Corresponding author. Address: Division of Applied Life Science (BK21), Graduate School, Gyeongsang National University, 900, Kaswa-dong, Jinju 660-701, South Korea. Tel.: +82 55 751 5466; fax: +82 55 757 0178.
E-mail address: pjkim@nongae.gsnu.ac.kr (P.J. Kim).

0045-6535/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2007.09.025

Recently there has been keen interest in the immobilization of heavy metals by using inorganic materials, such as lime, phosphate fertilizers and alkaline biosolid (Basta et al., 2001). These materials are found to be highly effective in reducing the bioavailability of metals in soils. Specially, addition of phosphate enhanced the immobilization of Cd in soils, thereby decreasing its phytoextractability. Two reasons could be attributed to phosphate-induced immobilization of Cd in soils: (i) precipitation of Cd as cadmium orthophosphate ($Cd_3(PO_4)_2$); and (ii) phosphate-induced Cd^{2+} adsorption. Results in the studies about the effect of phosphate fertilizer on reducing phytoavailability vary. A number of studies have examined the effect of phosphates on the immobilization of Cd in soils (Naidu et al., 1994; Jeanjean et al., 1995; Mandjiny et al., 1998; Bolan et al., 1999a). However, other studies reported that phosphate fertilizer in soil can increase the amount of cadmium available for plant uptake (Williams and David, 1973, 1976). In addition, more sufficient and accurate results on the feasibility of phosphate fertilizers for reducing the phytoavailability of Cd in field sites are scarce. The objective of this study was to investigate the effect of fused and super phosphate fertilizer on radish Cd uptake and Cd extractability in soil through field test. Fused and super phosphate (FSP) is a main phosphate fertilizer in Korea and was developed by mixing fused phosphate and super phosphate with a ratio of 5:1 on weight basis to control P release pattern.

Table 1
Physical and chemical properties of the soil before the test

Items	Concentration	Warning criteria[a]
pH (1:5 with H2O)	5.20	
Organic matter (g kg^{-1})	48.9	
Total nitrogen (g kg^{-1})	3.5	
Available phosphorus (mg kg^{-1})	101	
Cation exchange capacity ($cmol_c$ kg^{-1})	6.9	
Exchangeable cation ($cmol_c$ kg^{-1})		
K	0.17	
Ca	3.97	
Mg	0.87	
Na	0.03	
0.1 N HCl extractable heavy metals (mg kg^{-1})		
Cd	5.1	1.5
Cu	11.5	50
Pb	7.0	100
Zn	26.6	300
Cadmium fraction (mg kg^{-1})		
Water soluble	0.06 (0.99%)[b]	
Exchangeable + acidic	0.78 (12.4%)	
Reducible	1.58 (25.2%)	
Oxidizable	2.72 (43.4%)	
Residual	1.12 (17.8%)	
Total	6.26 (100%)	

Note: [a]means warning criteria of each heavy metals established by Korean Soil Environmental Conservation Act.
[b]() Means the percentage of each fraction concentration to total Cd.

2. Materials and methods

2.1. Soil and site description

For the field and incubation tests, an upland soil located on the downstream of *Bongsan* gold mine in *Hapcheon* council, *Gyeongnam* province, southern Korea (128°01′N and 34°37′E) was selected for this study. This soil is classified to belong to *Chilgog* series (a moderately well drained fine loamy Fluvaquentic Eutrudept) and contain 6.1% of clay, 35% of silt and 58.9% of sand (sandy loam). The surface soil (0–15 cm) was collected, air-dried, ground to pass through a 2 mm sieve, and stored in a plastic vessel prior to laboratory analysis and incubation test. Chemical properties of the soil used are described in Table 1. In this soil, Cd was the only heavy metal exceeding the warning criteria established by the Korean Soil Environmental Conservation Act (ME, 2005). Total and 0.1 N HCl extractable Cd concentrations were about 6.3 and 5.1 mg kg^{-1}, respectively (Table 1). Most of the Cd was in the reducible (Fe, Mn oxide bound form) and oxidizable phase (organic matter bound form) and about 13% of the total Cd existed in available forms (water soluble and exchangeable + acidic phase).

2.2. Field test

To evaluate the effect of phosphate fertilizer on plant Cd uptake, FSP and radish (*Raphanus sativa* L.) were selected as a target fertilizer and test crop. Four levels (0, 33.5, 167.5 and 335 kg P ha^{-1}) of FSP on the basis of the recommendation level (33.5 kg P ha^{-1}) of phosphate for radish, were applied before planting. The plots were arranged in a completely randomized design with three replication. Individual plot size was 1 m wide and 2 m long. Radish seed were sown by hand at intervals of 20 cm × 15 cm on September 9, 2004 and harvested on November 20 in the same year. According to the crop cultivation guideline (RDA, 1999), chemical fertilizers N (180 kg ha^{-1}) and KCl (128 kg ha^{-1}) and lime as $Ca(OH)_2$ (2 Mg ha^{-1}) were applied together with manure (30 Mg ha^{-1}) to all plots before planting.

2.3. Incubation test

In the field test, Cd uptake of radish and Cd extractability in soil were found to increase with increasing FSP fertilization level. Other soil managing factors such as fertilization, liming and compost amendment in the field test may affect on Cd dynamics in soil and Cd uptake of radish. For example, dissolved organic carbon (DOC) increased by compost application can make a complex with Cd and increase Cd mobility in soil and Cd uptake of plants (Hamon et al., 1995; Guisquiani et al., 1998). The increase of soil pH by liming can significantly decrease Cd solubility and decrease Cd uptake of radish (Hong et al., 2007). However, because FSP application level was