



Fractionation and solubility of cadmium in paddy soils amended with porous hydrated calcium silicate

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Abstract

Previous studies have shown that porous hydrated calcium silicate (PS) is very effective in decreasing cadmium (Cd) content in brown rice. However, it is unclear whether the PS influences cadmium transformation in soil. The present study examined the effect of PS on pH, cadmium transformation and cadmium solubility in Andosol and Alluvial soil, and also compared its effects with CaCO₃, acidic porous hydrated calcium silicate (APS) and silica gel. Soil cadmium was operationally fractionated into exchangeable (Exch), bound to carbonates (Carb), bound to iron and manganese oxides (FeMnO_x), bound to organic matters (OM) and residual (Res) fraction. Application of PS and CaCO₃ at high rates enhanced soil pH, while APS and silica gel did not obviously change soil pH. PS and CaCO₃ also increased the FeMnO_x-Cd in Andosol and Carb-Cd in Alluvial soil, thus reducing the Exch-Cd in the tested soils. However, PS was less effective than CaCO₃ at the same application rate. Cadmium fractions in the two soils were not changed by the treatments of APS and silica gel. There were no obvious differences in the solubility of cadmium in soils treated with PS, APS, silica gel and CaCO₃ except Andosol treated 2.0% CaCO₃ at the same pH of soil-CaCl₂ suspensions. These findings suggested that the decrease of cadmium availability in soil was mainly attributed to the increase of soil pH caused by PS.

Key words: porous hydrated calcium silicate; solubility; soil cadmium

Introduction

Cadmium is one of toxic and easily mobile elements in the environment. Although it occurs naturally in a very small amount in soils, soil cadmium has been increased by atmospheric deposition and human activities such as mining, application of organic and inorganic fertilizers or sewage sludge, and wastewater irrigation (McLaughlin *et al.*, 1999). As a result, soils have been polluted by cadmium in some areas and some plants grown on those soils contained high amounts of cadmium. This can be very harmful to higher trophic organisms and eventually to humans due to the biomagnification of elements within the food chains. Since “itai-itai” disease was reported in Japan in the middle of 20th century, soil polluted by cadmium and its remediation have aroused worldwide attention (Chen *et al.*, 2000). *In situ* remediation of cadmium-polluted soils involves stabilizing cadmium in soils by soil additives or removing cadmium from soils by plants (Ernst, 1996; Chaney *et al.*, 1997; Mckinley *et al.*, 2001). These techniques are cost-effective and environmental friendly, and suitable for lightly polluted agricultural soils. Nowadays, the effects of several additives on cadmium stabilization in soils have been tested: for example, lime

(Hooda and Alloway, 1996; Chen *et al.*, 2000; Mckinley *et al.*, 2001; Singh and Myhr, 1998), hydroxyapatite (Laperche *et al.*, 1996; Boisson *et al.*, 1999; Hettiarachchi and Pierzynski, 2002), zeolite (Gworek, 1992; Lin *et al.*, 1998; Oste *et al.*, 2002), beringite (Vangronsveld *et al.*, 1996; Lombi *et al.*, 2002), steel shots (Chen *et al.*, 2000; Mench *et al.*, 1994) and Fe or Mn oxides (Chlopecka and Adriano, 1997; Hettiarachchi and Pierzynski, 2002; Mann and Ritchie, 1995).

Porous hydrated calcium silicate (PS) is an industrial waste of autoclave light weight concrete, with the main component as tobermorite which can react with H₂O and CO₂ to produce carbonate and silica gel in soils (Saigusa *et al.*, 2000). Compared with silicate fertilizers derived from slag, PS is more effective in increasing silicon content of rice, and therefore used as a kind of silicon fertilizer in the rice production of Japan (Saigusa *et al.*, 1998). PS has also been found to decrease cadmium content in brown rice (Hasegawa *et al.*, 1995). Our previous study showed that PS increased the sorption capacity of cadmium by soils (Zhao and Saigusa, 2004). However, it is unclear whether applying PS alters cadmium forms in soil.

Cadmium exists in soil in a number of physico-chemical forms with different availability to plants. Thus, the changes in cadmium forms in soils show some information on the mechanism of cadmium stabilization after application of soil additives. Sequential extraction procedures

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have been widely used for examining the physico-chemical forms of heavy metals in soils. Although these procedures are often criticized because of their complexity and difficulty in interpretation and some potential problems such as lack of specificity of extractants and readsorption of metals during extraction, it can provide useful information on metal distribution in soils, especially for a comparative purpose (McLaren and Clucas, 2001).

The purpose of this study was to investigate the influences of porous hydrated calcium silicate (PS) on the chemical forms of native or added cadmium in paddy soils. The solubility of cadmium in soil at different pH was also investigated. Additives such as acidified porous hydrated calcium silicate (APS), lime and silica gel was also included for comparison.

1 Materials and methods

1.1 Pot experiment

Andosol and Alluvial soils were collected from the 0–20 cm soil depth of paddy fields, Japan. Soils were air-dried, crushed and passed through a 5-mm sieve. Clay, organic matter, cadmium contents were 193.6 g/kg, 59.1 g/kg, 0.33 mg/kg for Andosol and 215.8 g/kg, <10 g/kg, 1.05 mg/kg for Alluvial soil. Andosol and Alluvial soils had pH of 5.58 and 5.44, respectively. Air-dried soils (2.5 kg) were mixed with 7.15 g of slow released fertilizer (14-20-14), soil additives and 1.5 L of water, then were into a polyvinyl pot. The PS was applied at rates of 0.2%, 0.5%, 1.0% and 2.0%. The application rate was 2.0% for APS and CaCO₃, and 1.0% for silica gel. Some properties of the soil additives are shown in Table 1. For Andosol, cadmium level was brought to 7 mg/kg by adding CdCl₂ solution to the soil. The experiment was arranged randomly. Each treatment had four replications. After equilibration for one week, three rice seedlings (*Orzya sativa* L. var. Hitomebore) were transplanted in each pot. The experiment was carried out till the harvest stage. Throughout the experiment, the water level was kept 4 cm above the soil surface. After harvest, soils from each treatment were sampled, air-dried and ground to pass through a 2-mm sieve, then kept for analysis.

Table 1 Properties of the soil additives used in the study

Soil additives	pH	CaO (%)	SiO ₂ (%)	CaSO ₄ (%)
PS	10.1	21.7	52.9	1.3
APS	4.6	-	37.1	39.8
Silica gel	3.93	-	>80.0	-
CaCO ₃	9.5	40.0	-	-

PS: Porous hydrated calcium silicate; APS: acidic porous hydrated calcium silicate.

1.2 Sample analysis

Cadmium fractionation was performed following Chlopecka's method (1996), which was based on the report of Tessier *et al.* (1979). This procedure partitions the heavy metals into five operationally defined chemical fractions: exchangeable (Exch), bound to carbonates (Carb), bound to iron and manganese oxides (FeMnO_x), bound to organic matters (OM) and residual (Res) (McGrath *et al.*, 2001).

Soil properties were measured following the methods described by the Edit Committee of Analysis Method of Soil Environment of Japan (1997). Soil pH was measured in a 1:2.5 (soil:water) slurry using a combination electrode. Organic C was determined by ignition method. Silt and clay content was determined by the pipette method. Total cadmium was determined by atomic absorption spectroscopy (Hitachi 180, Japan) following H₂SO₄-HNO₃-HClO₄ digestion.

The solubility of soil cadmium response to pH was investigated by the modified method of Martínez and Motto (2000). Briefly, 2.00 g of soils, with three replications, were weighed and put into a 50-ml centrifuge tube containing 20 ml of 0.05 mmol/L CaCl₂. Acid (HCl) or alkaline (NaOH) was added to adjust the pH of the suspension. The amount of acid or alkaline was determined by a preliminary experiment. To minimize the volume changes of soil-0.05 mmol/L CaCl₂ suspension, the amount of acid or alkaline was kept less than 1 ml by increasing the concentration of acid or alkaline. The suspension was shaken for 24 h at 80 r/min. The suspension was centrifuged for 30 min at 12000×g, filtered. Cadmium in the filtrate was determined by atomic absorption spectroscopy. The final pH of the suspension was measured and used to interpret the metal solubility.

2 Results and discussion

2.1 Soil pH changes

The pH of soils treated with soil additives was determined at the end of experiment (Table 2). The change of soil pH depended on the amounts and the properties of soil additives. APS and silica gel, as acidic materials, did not decrease the pH in two soils, while PS and CaCO₃ increased soil pH obviously. The pH values in the two soils tended to increase with the PS amount applied. However, PS was less effective than CaCO₃ in increasing soil pH at the same rate.

2.2 Transformation of cadmium forms in soil

The fractions and contents of cadmium in soils are present in Fig.1. Without soil additives, the amounts of

Table 2 Soil pH at the end of experiment

	pH							
	Control	PS 0.2%	PS 0.5%	PS 1.0%	PS 2.0%	CaCO ₃ 2.0%	APS 2.0%	Silica gel 1.0%
Andosol soil	5.58	5.69	5.84	6.07	6.56	7.38	5.56	5.60
Alluvial soil	5.44	5.66	6.21	6.66	7.34	7.54	5.61	5.35

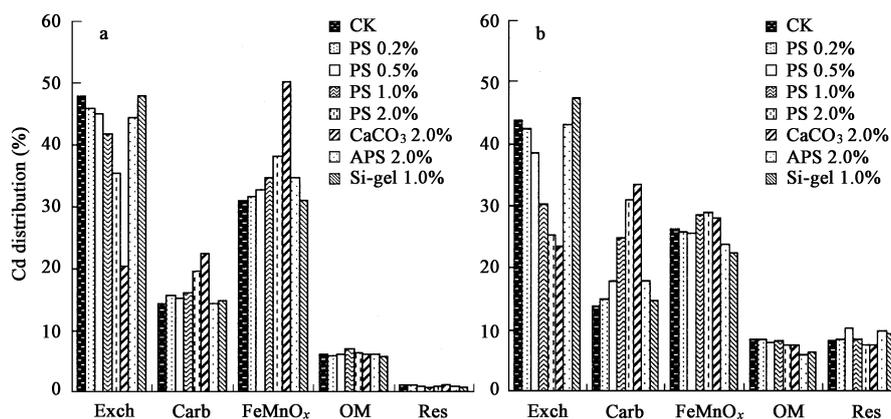


Fig. 1 Distribution of Cd in Andosol (a) and Alluvial (b) soils affected by soil additives.

cadmium fractions followed the order: Exch > FeMnO_x > Carb > OM > Res, showing that cadmium (either native cadmium or exotic cadmium) existed mainly as exchangeable, carbonate bound and Fe-Mn oxide bound forms in the two soils. Exch-Cd, FeMnO_x-Cd and Carb-Cd in soils have been reported to be mobile cadmium, which may be available to plants when the conditions were suitable (Chlopecka, 1996). The sum of the three forms was about 90% of the total in Andosol and 84% of the total in Alluvial soils. The high percentages of mobile cadmium in soils have also been reported by other researchers who used the method of Tessier *et al.* (1979). For examples, Narwal and Singh (1998) reported that the highest amount of cadmium was present in the exchangeable fraction. Theodoratos *et al.* (2000) found that the sum of cadmium in 1 mol/L MgCl₂ and 1 mol/L NH₄OAc (pH 5.0) was 60% of the total. Li and Thornton (2001) observed that the first three fractions (Exch, FeMnO_x and Carb) accounted for more than 70% of the total in soils at a smelting site, and the exchangeable cadmium alone was 7%–52% of the total. The very low percentage of residual cadmium in Andosol showed that cadmium in soil was still mobile even though the soil had been incubated for five months after cadmium application.

The distribution patterns of cadmium in Andosol were not obvious affected by the treatments of PS 0.2%, PS 0.5%, PS 1.0%, APS 2.0% and silica gel 1.0%. However, treatments with PS 2.0% and CaCO₃ 2.0% decreased the exchangeable cadmium by 26% and 57% while increased cadmium bound to carbonate by 36% and 56%, respectively, as those of the control. Cadmium bound to Fe-Mn oxide was also increased by 23% and 56% over the control by PS 2.0% and CaCO₃ 2.0%, respectively. This meant a conversion of exchangeable cadmium to carbonate and Fe-Mn oxide associated forms. PS was less effective than CaCO₃ in transformation of cadmium forms in soils at the same application rate.

Similarly, the distribution of cadmium in Alluvial soil was not significantly influenced by the treatments of PS 0.2%, PS 0.5%, APS 2.0% and silica gel 1.0%, but affected by the treatments of PS 1.0%, PS 2.0% and CaCO₃

2.0%. Compared to the control, the exchangeable cadmium decreased by 31%, 43% and 47%, whereas cadmium bound to carbonate increased by 81%, 118% and 149% for the PS 1.0%, PS 2.0% and CaCO₃ 2.0% treatment, respectively; also indicating less effectiveness of PS than CaCO₃. Although cadmium bound to Fe-Mn oxide was the highest in the treatment with PS 2.0%, there were no significant differences among treatments.

The current results showed that soil additives mainly influenced the three forms: exchangeable, carbonate and Fe-Mn oxide forms in soils, being in agreement with those of Chlopecka and Adriano (1997). However, the effect depended on the properties of soil additives. PS and lime treatment, which increased soil pH, resulted in a decrease of exchangeable cadmium, and an increase of cadmium associated with carbonate and Fe-Mn oxides. On the other hand, APS and silica gel, which are the products of PS transformation in soils, did not obviously affect the distribution of cadmium in both soils, which has also been demonstrated in other studies (Chlopecka and Adriano, 1997; Tu *et al.*, 2000). The effects of soil additives on cadmium forms in soils also depend on the properties of soils. Cadmium associated with Fe-Mn oxide in Andosol was increased by PS and lime treatment, while that of sandy Alluvial soil was not obviously changed.

2.3 Solubility of soil cadmium verse pH

Of any single factor, soil pH generally has the greatest impact on the solubility or retention of metals in soils, with a greater retention and lower solubility of metal cations occurring at high soil pH (Martínez and Motto, 2000). As shown in Fig.2, the amount of cadmium released from soils decreased with the increasing pH of soil-0.05 mol/L CaCl₂ suspension. The changes in the cadmium solubility with the pH of soil-0.05 mol/L CaCl₂ suspension did not differ between the untreated and treated soils with silica gel, APS, PS 1.0% and PS 2.0%. In the case of CaCO₃, cadmium solubility was no difference between the treated and untreated Alluvial soil at the same final pH, but a little lower in treated than untreated Andosol. This was in agreement with the results of the sequential extraction.

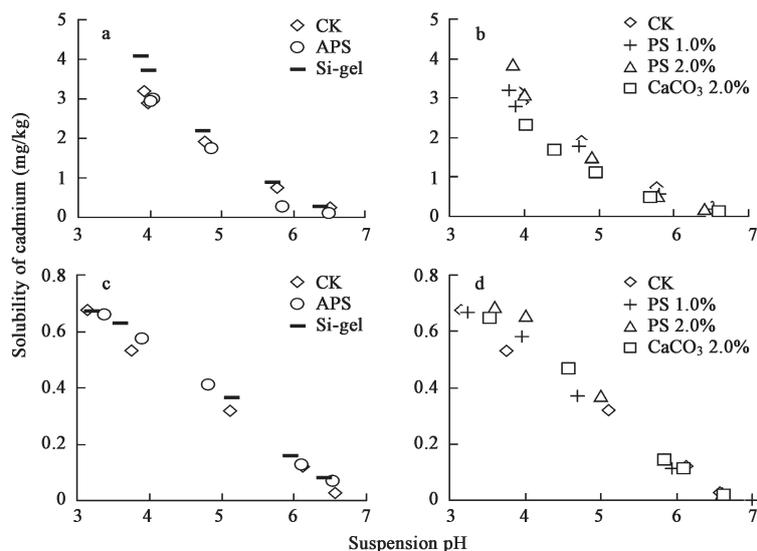


Fig. 2 Solubility of soil cadmium vs. suspension pH. (a) and (b) in Andosol soil; (c) and (d) in Alluvial soil.

3 Conclusions

Porous hydrated calcium silicate was able to enhance soil pH, improve the portion of $\text{FeMnO}_x\text{-Cd}$ in Andosol soil and Carb-Cd in Alluvial soil, and reduce the Exch-Cd in the tested soils. However, PS was less effective than CaCO_3 in converting exchangeable cadmium to $\text{FeMnO}_x\text{-Cd}$ or Carb-Cd at the same application rate. There were no significant differences in the cadmium solubility among treatments with PS, APS, silica gel and CaCO_3 at the same pH of soil- CaCl_2 suspensions. This implied that the decrease of cadmium availability in soil was mainly attributed to the increase of soil pH caused by PS addition.

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References

- Boisson J, Ruttens A, Mench M *et al.*, 1999. Evaluation of hydroxyapatite as a metal immobilizing soil additive for the remediation of polluted soils: Part 1. Influence of hydroxyapatite on metal exchangeability in soil, plant growth and plant metal accumulation[J]. *Environment Pollution*, 104: 225–233.
- Chaney R L, Malik M, Li Y M *et al.*, 1997. Phytoremediation of soil metals[J]. *Current Opinion in Biotechnology*, 8: 279–284.
- Chen H M, Zheng C R, Tu C *et al.*, 2000. Chemical methods and phytoremediation of soils contaminated with heavy metals[J]. *Chemosphere*, 41: 229–234.
- Chlopecka A, Adriano D C, 1996. Mimicked *in-situ* stabilization of metals in cropped soil: bioavailability and chemical form of zinc[J]. *Environ Sci Technol*, 30: 3294–3303.
- Chlopecka A, 1996. Assessment of form of Cd, Zn and Pb in contaminated calcareous and gleyed soils in Southwest Poland[J]. *Science Total Environment*, 188: 253–262.
- Chlopecka A, Adriano D C, 1997. Influence of zeolite, apatite and Fe-oxide on cadmium and Pb uptake by crops[J]. *Science Total Environment*, 207: 195–206.
- Ernst W H O, 1996. Bioavailability of heavy metals and decontamination of soils by plants[J]. *Applied Geochemistry*, 11: 163–167.
- Gworek B, 1992. Inactivation of cadmium in contaminated soils by synthetic zeolites[J]. *Environmental Pollution*, 75: 269–271.
- Hasegawa E, Shima H, Saitou M *et al.*, 1995. Effect of autoclaved light weight concrete on suppression of cadmium uptake by rice plants in clay paddy fields[J]. *Bulletin Miyagi Prefecture Agric Research Centre*, 61: 13–32.
- Hettiarachchi G M, Pierzynski G M, 2002. *In situ* stabilization of soil lead using phosphorus and manganese oxide: influence of plant growth[J]. *J Environ Quality*, 31: 564–572.
- Hooda P S, Alloway B J, 1996. The effect of liming on heavy metal concentrations in wheat, carrots and spinach grown on previously sludge-applied soils[J]. *J Agricultural Science*, 127: 289–294.
- Laperche V, Traina S J, Gaddam P *et al.*, 1996. Chemical and mineralogical characterizations of Pb in a contaminated soils: reactions with synthetic apatite[J]. *Environ Sci Technol*, 30: 3321–3326.
- Li X, Thornton I, 2001. Chemical partitioning of trace and major elements in soils contaminated by mining and smelting activities[J]. *Applied Geochemistry*, 16: 1693–1706.
- Lin C F, Lo S S, Lin H Y *et al.*, 1998. Stabilization of cadmium contaminated soils using synthesized zeolite[J]. *Journal Hazardous Material*, 60: 217–226.
- Lombi E, Zhao F J, Zhang G Y *et al.*, 2002. *In situ* fixation of metals in soils using bauxite residue: chemical assessment[J]. *Environment Pollution*, 118: 435–443.
- Mann S S, Ritchie G S P, 1995. Forms of Cd in sandy soils after amendment with soils of higher fixing capacity[J]. *Environment Pollution*, 87: 23–29.
- Martínez C E, Motto H L, 2000. Solubility of lead, zinc and copper added to mineral soils[J]. *Environment Pollution*, 107: 153–158.
- McGrath S P, Zhao F J, Dunham S J *et al.*, 2000. Long-term changes in extractability and bioavailability of zinc and cadmium after sludge application[J]. *Journal Environmental Quality*, 29: 875–883.
- Mckinley J D, Thomas H R, Williams K P *et al.*, 2001. Chemical

- analysis of contaminated soils strengthened by addition of lime[J]. *Engineering Geology*, 60: 181–192.
- McLaren R G, Clucas L M, 2001. Fractionation of copper, nickel and zinc in metal-spiked sewage sludge[J]. *Journal Environmental Quality*, 30: 1968–1975.
- McLaughlin M J, Parker D R, Clarke J M, 1999. Metals and micronutrients-food safety[J]. *Field Crops Research*, 60: 143–163.
- Mench M, Vangronsveld J, Didier V *et al.*, 1994. Evaluation of metal mobility, plant availability and immobilization by chemical agents in a limed silty soil[J]. *Environment Pollution*, 86: 279–286.
- Narwal R P, Singh B R, 1998. Effect of organic materials on partition, extractability and plant uptake of metals in an alum shale soil[J]. *Water Air & Soil Pollution*, 103(1-4): 405–421.
- Oste L A, Lexmond T M, van Riemsdijk W H, 2002. Metal immobilization in soils using synthetic zeolites[J]. *J Environmental Quality*, 31: 813–821.
- Saigusa M, Yamamoto A, Shibuya K, 2000. Change of structure of porous hydrated calcium silicate by dissolution in paddy soil[J]. *Soil Science Plant Nutrition*, 46: 89–95.
- Saigusa M, Yamamoto A, Shibuya K, 1998. Agricultural use of porous hydrated calcium silicate, II. Practical use to improve silicon nutrition of rice plants in paddy fields[J]. *Japanese Journal Soil Science Plant Nutrition*, 69: 612–617.
- Singh B R, Myhr K, 1998. Cadmium uptake by barley as affected by Cd sources and pH levels[J]. *Geoderma*, 84: 185–194.
- Tessier A, Campbell P G C, Bisson M, 1979. Sequential extraction procedure for the speciation of particulate trace elements[J]. *Analysis Chemistry*, 51: 844–851.
- The Edit Committee of Analysis Methods of Soil Environment. 1997. *Analysis methods of soil environment*[M]. Tokyo: Hakuyuu Press.
- Theodoratos P, Moirou A, Xenidis A *et al.*, 2000. The use of municipal sewage sludge for the stabilization of soils contaminated by mining activities[J]. *J Hazardous Materials*, B77: 177–191.
- Tu C, Zheng C R, Chen H M. 2000. Effect of applying chemical fertilizers on forms of lead and cadmium in red soil[J]. *Chemosphere*, 41: 133–138.
- Vangronsveld J, Colpaert J V, van Tichelen K K, 1996. Reclamation of a bare industrial area contaminated by non-ferrous metals: physico-chemical and biological evaluation of the durability of soil treatment and revegetation[J]. *Environmental Pollution*, 94: 131–140.
- Zhao X L, Saigusa M, 2004. Effect of porous hydrated calcium silica on sorption and desorption of cadmium by soils[J]. *Soil Science and Plant Nutrition*, 50(3): 315–319.