Mechanism of cadmium immobilization in phosphate-amended arable soils

Chuanpit Ruangcharus1†, Sung Un Kim1† and Chang Oh Hong1,2*

Abstract

Little is known about the exact mechanism of cadmium (Cd) immobilization by phosphate (P) in arable soil containing low Cd concentration. This study was designed to describe this mechanism in detail. We determined the phosphorus (P) addition rate allowing Cd to precipitate as Cd minerals in Cd-contaminated arable soils and identified the main species of Cd minerals formed by the reaction of Cd and P, using the chemical equilibrium model MINTEQ. To determine the amount of Cd adsorption to soil adsorbed P, 0–10,000 mg PL\(^{-1}\) of K\(_2\)HPO\(_4\) solution was reacted with soil, then the P adsorbed soil was reacted with a CdCl\(_2\) solution (500 mg Cd L\(^{-1}\)). Cadmium might not precipitate as Cd minerals such as Cd\(_3\)(PO\(_4\))\(_2\) and CdCO\(_3\) with a recommended application rate of P fertilizer in field scale. Cadmium might be immobilized by Cd\(^{2+}\) adsorption instead of precipitation under a low P application system. Phosphate adsorption increased the negative charge of soil and Cd adsorption. The contributions of the increase in pH- and P-induced negative charges to the total increase in the soil negative charge were 93.2 and 6.8%, respectively. The increase in Cd adsorption caused by P adsorption was mainly attributed to the increase in pH-induced negative charge.

Keywords: Adsorption, Negative charge, Precipitation, Soil pH, Speciation

Introduction

Various remediation technologies have been applied to cadmium (Cd)-contaminated arable soils to make the crops grown in these soils suitable for human consumption [1–6]. Many studies on Cd chemical immobilization in arable soils using phosphate (P) fertilizer have been conducted. It is well known that P materials are effective in reducing the bioavailability of Cd in soils [7–11].

The immobilization of Cd with P compounds in soils is caused by various mechanisms: (i) the formation of Cd minerals such as Cd\(_3\)(PO\(_4\))\(_2\); (ii) Cd\(^{2+}\) adsorption induced by P; (iii) cation exchange; and (iv) surface complexation. Indeed, several studies observed that Cd was immobilized with P through forming a compound mineral with varying concentrations of these two elements. However, others reported that the precipitation of a Cd-P mineral did not occur under their experimental conditions [12, 13]. Some researchers reported that the addition of P immobilized Cd by increasing its adsorption onto the surface of soil colloids [4, 14, 15], but did not elucidate the exact pathway of P-induced Cd\(^{2+}\) adsorption. In a previous study [4], we suggested that Cd might not be precipitated as Cd-P minerals under 1,600 mg P kg\(^{-1}\) of P addition in soil containing low Cd concentration (total Cd: 5.57 mg kg\(^{-1}\)). In such soil conditions, an increase in the pH-induced negative charge of soil could play an important role in the immobilization of Cd. However, we did not determine the soil condition under which Cd could precipitate with P addition and did not investigate the exact role of a pH-induced negative charge in Cd immobilization. So far, the exact mechanism of Cd immobilization with P in arable soils containing low Cd concentration remains poorly understood.

Therefore, this study was designed to investigate the mechanism of Cd immobilization by P in the arable soil...
containing low Cd concentration, by estimating (1) the P addition rate under which Cd could precipitate as a Cd-P mineral and identify the main species of Cd minerals formed by the reaction of Cd and P; (2) the contribution of negative charge induced by P to Cd\(^{2+}\) adsorption in soil.

**Materials and methods**

**Incubation test for the precipitation of cadmium and phosphate**

An arable soil located near the Bongsan gold mine area in Hapcheon, South Korea (128°01′N and 34°37′E) was collected for the precipitation test. The total Cd concentration in this soil was 5.57 mg kg\(^{-1}\), which exceeded the warning criteria for Cd in the arable soil established by the Korean Soil Environmental Conservation Act [16]. The chemical and physical properties of the collected arable soil are shown in Table 1.

To determine the suitable P addition rate to induce Cd precipitation as Cd-P minerals, the effects of P addition rate on the solubility of Cd minerals were investigated in this study. A 500-g soil sample was mixed with 0, 200, 400, 800, 1600, 3200, 8000, and 16,000 mg P kg\(^{-1}\) of K\(_2\)HPO\(_4\) in a plastic beaker and placed in the dark at 25 °C for 8 weeks. Distilled water was added to fill up 70% of the soil pore volume. Soil water content was maintained by periodically weighing the beakers and adjusting the weight by adding distilled water. Triplicates were arranged in a completely randomized design in an incubator.

**Phosphate adsorption**

For the P and Cd adsorption test, uncontaminated arable soil was collected from the experimental farm of Pusan National University, Miryang, South Korea (128°43′N and 35°30′E). The physical and chemical properties of the studied soil are also given in Table 1.

To adsorb P onto the uncontaminated soil, a 1-g soil sample was reacted with 20 ml of 0–10,000 mg P L\(^{-1}\) (K\(_2\)HPO\(_4\)) solution without controlling solution pH and shaken at 25 °C for 48 h. Solution pH condition is a significant factor affecting adsorptions of P and Cd. We assumed that results of the test could be derived from the wrong thing, if adsorption test was conducted in controlled pH condition. For this reason, solution pH was not controlled in the test. The amount of P adsorbed was calculated by subtracting its final concentration in the equilibrium solution from its initial concentration. After shaking for 48 h, the soil residues were rinsed with 20 ml of 95% ethyl alcohol; three replicates were used to analyze for the negative charge of the soil and the other three were used to measure the amount of adsorbed Cd.

**Cadmium adsorption**

The soil residues mentioned earlier were reacted with 20 ml of 500 mg Cd L\(^{-1}\) (CdCl\(_2\)) solution and shaken at 25 °C for 48 h to determine the amount of Cd adsorbed by P fixed to the soil. The Cd adsorption capacity was calculated by subtracting its final concentration in the equilibrium solution from its initial concentration.

**Determination of pH-induced negative charge and phosphate-induced negative charge**

The amount of Cd adsorbed to P added to the soil could be dependent on the change in soil negative charge brought about by P adsorption. An increase in the negative charge of the soil caused by P adsorption could be attributed to corresponding increases in (1) the pH-dependent charge by specific adsorption of P (pH-induced negative charge) and (2) negative charge from adsorbed orthophosphate (P-induced negative charge). Therefore, we determined the contribution of each of the pH-induced negative charge and P-induced negative charge to the total increase in negative charge of the soil elicited by P adsorption.

The soil used for the P and Cd adsorption test was used to determine the contribution of pH-induced negative charge in the soil. 25 ml of distilled water was added to 5 g of the soil and shaken in a polyethylene centrifuge

### Table 1 Selected chemical and physical properties of soil for precipitation and adsorption test

| Items                          | Cd-contaminated soil for precipitation test | Uncontaminated soil for adsorption test |
|-------------------------------|---------------------------------------------|-----------------------------------------|
| pH (1:5 with H\(_2\)O)        | 5.20                                        | 6.97                                    |
| Organic matter (g kg\(^{-1}\))| 48.9                                        | 10.2                                    |
| Available phosphorus (mg kg\(^{-1}\)) | 10.1                                       | 25.3                                    |
| Cation exchange capacity (cmol\(_{\text{eq}}\) kg\(^{-1}\)) | 6.9                                        | 11.9                                    |
| Exchangeable cation (cmol\(_{\text{eq}}\) kg\(^{-1}\)) |                               |                                         |
| K                             | 0.17                                        | 0.9                                     |
| Ca                            | 3.97                                        | 7.8                                     |
| Mg                            | 0.87                                        | 0.9                                     |
| Particle size distribution (%) |                                             |                                         |
| Clay                          | 6.1                                         | 16.4                                    |
| Silt                          | 35.0                                        | 23.3                                    |
| Sand                          | 58.9                                        | 55.4                                    |
| Soil texture                   | Sandy loam                                  | Clay loam                               |
| Total Cd (mg kg\(^{-1}\))     | 5.57                                        | tr                                      |
| 1 M NH\(_4\)OAc extractable Cd (mg kg\(^{-1}\)) | 1.45                                        | tr                                      |
tube at 25 °C until the pH was adjusted to pH between 3 and 10 using either 0.1 M NaOH or HCl. After centrifuging for 10 min at 5000 rpm, the supernatant solutions were decanted and 20 ml of 95% ethyl alcohol was added to rinse the soils before analyzing the pH-induced negative charge of the soil.

The phosphate-induced negative charge was calculated by subtracting pH-induced negative charge obtained at equilbrial P adsorption from the total negative charge attained at P adsorption equilibrium.

**Cd-mineral speciation**

The Visual MINTEQ (ver 2.23) was used to predict the precipitation or dissolution of Cd minerals such as Cd₃(PO₄)₂, CdCO₃, and Cd(OH)₂. The input parameters were the respective concentrations of cations and anions in the soil solution. The concentration of dissolved organic carbon (DOC), ionic strength, pH, and temperature (25 °C) were also inputted. In this study, we assumed a constant CO₂ concentration of 0.003 atm.

**Chemical analysis**

The chemical properties of the collected soils (< 2 mm) were analyzed using the following methods: pH (1:5 with H₂O), organic matter content [17], and concentrations of exchangeable Ca²⁺, Mg²⁺, and K⁺ (1 M NH₄-acetate pH 7.0, AA, Shimazu 660). The available P content was determined using the Lancaster method [18]. The negative charge of the soil was measured using 0.1 M NaCl after performing Schofield’s ion retention method [19]. The concentrations of cations in the soil solution were quantified using an inductively coupled plasma-optical emission spectrophotometer (ICP-OES, Perkin Elmer Model OPTIMA 4300 DV, Shelton USA). DOC was quantified using a TOC analyzer (Total Organic Carbon Analyzer Shimadzu Model TOC-VCPN, Japan).

After the P adsorption test, the pH of the reacted solution was measured using a pH meter. The concentration of P in the equilibrium solution was measured spectrophotometrically at 880 nm [20]. After the Cd adsorption test, Cd concentration in the equilibrium solution was measured using ICP-OES.

**Results and discussion**

**Precipitation of cadmium with phosphate**

The pH of the soil solution increased with increasing K₂HPO₄ concentrations (Table 2). That was because the hydroxyl (OH⁻) group was released into the soil solution when the specific adsorption of P to the edge of the crystals of clay minerals occurred. Log activity of CO₃²⁻ increased significantly as more K₂HPO₄ was added, corresponding to an increase in soil pH. The dissociation of carbonic acid in the soil solution is represented in the following equation:

\[
H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow H^+ + CO_3^{2-}
\]  \hspace{1cm} (1)

where pKₐ₁ and pKₐ₂ in carbonic acid are 6.36 and 10.33, respectively. Very few cadmium carbonate (CdCO₃) molecules can form in acidic soil as the activity of CO₃²⁻ is low, but this increases in alkaline soil, allowing more CdCO₃ molecules to form [21]. The log activity of H₃PO₄ increased up to the peak concentration of 1600 mg P kg⁻¹, but decreased afterwards as more K₂HPO₄ was added (Table 2). This change is related to an increase in soil pH as more K₂HPO₄ is added. The dissociation of phosphoric acid in soil solution is represented in the following equation:

\[
H_3PO_4 \leftrightarrow H^+ + H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}
\]  \hspace{1cm} (2)

where pKₐ₁, pKₐ₂, and pKₐ₃ of phosphoric acid are 2.15, 7.20, and 12.35, respectively. Therefore, H₃PO₄ is the predominant chemical species of phosphoric acid in the pH range of 2.15–7.20. However, H₂PO₄⁻ dominates above pH 7.20 [21]. The log activity of H₂PO₄⁻ increased up to 1,600 mg P kg⁻¹ as more K₂HPO₄ was added, as the solution pH was below 7.20 (and hence H₂PO₄⁻ was predominant) (Table 2). However, it decreased when we added more than 1,600 mg P kg⁻¹ of K₂HPO₄, as soil pH increased above 7.20, in which HPO₄²⁻ is predominant.

The results from the calculated Cd solubility diagram (Fig. 1) suggest that CdCO₃ might control the solubility of Cd at 8000 mg P kg⁻¹ of K₂HPO₄ addition. When pH exceeds 7.5; depending on CO₂ (g), Cd²⁺ activity is limited by CdCO₃ concentration [21]. Soil pH was 8.29 with 8000 mg P kg⁻¹ of K₂HPO₄ addition (Table 2) and the soil

| K₂HPO₄ addition (mg P kg⁻¹) | pH | Ionic strength (M) | log activity (mol L⁻¹) |
|-----------------------------|----|-------------------|-----------------------|
|                             |    |                   |                      |
| 0                           | 5.20 | 0.019             | -5.614 -5.571 -9.426 |
| 400                         | 5.97 | 0.066             | -7.202 -3.165 -7.679 |
| 800                         | 6.42 | 0.097             | -7.469 -2.570 -6.828 |
| 1600                        | 7.03 | 0.117             | -7.878 -1.787 -5.799 |
| 3200                        | 7.46 | 0.286             | -7.795 -1.992 -4.841 |
| 8000                        | 8.29 | 0.772             | -7.438 -2.543 -3.624 |
| 16000                       | 8.94 | 1.543             | -7.128 -2.955 -2.097 |

Table 2 Calculated activities of Cd²⁺, H₂PO₄⁻, and CO₃²⁻, as well as the ionic strength and pH of soil solutions amended with different rates of K₂HPO₄ after eight weeks of incubation.
solution was supersaturated with respect to only CdCO₃. However, the soil solution was supersaturated with respect to both CdCO₃ and Cd₃(PO₄)₂ under 16,000 mg P kg⁻¹ of P addition (Fig. 1). In general, ions in a given solution can precipitate if the IAP of ion-induced minerals is higher than the mineral solubility product (Ksp) [22].

Log IAP values of Cd₃(PO₄)₂ were −30.7 with 16,000 mg P kg⁻¹ of K₂HPO₄ addition and higher than Ksp values (−32.6) of Cd₃(PO₄)₂. This implies that Cd might precipitate as Cd₃(PO₄)₂ under 16,000 mg P kg⁻¹ conditions. Some studies reported formation of Cd₃(PO₄)₂ in Cd-contaminated soils amended with a suitable concentration of P [23, 24]. The application of large amounts of P fertilizer can release P from the arable land and subsequently, cause eutrophication of nearby water bodies. For instance, a concentration of 33.5 kg P ha⁻¹ of P fertilizer is recommended for radish cultivation in Korea [25], using a product concentration of ca. 18.6 mg P kg⁻¹. In this study, the soil solution was undersaturated compared to Cd₃(PO₄)₂ and CdCO₃ below 400 mg P kg⁻¹ (low P addition) and Cd might not precipitate as Cd₃(PO₄)₂ or CdCO₃ (Fig. 1). As a result, Cd solubility might be controlled by other mechanisms rather than precipitation under low P application systems.

**Phosphate adsorption**

Soil phosphate adsorption increased as the P equilibrium concentration increased (Fig. 2). In general, the P adsorption occurred with an L-curve type on the soil surface in the controlled pH condition. However, a C-curve type of P adsorption was observed in this study, probably due to changes in the soil solution pH depending on the concentration of K₂HPO₄. In this study, the P adsorption experiment was conducted without controlling solution pH to understand P dynamics under the natural soil condition in which P is specifically adsorbed or precipitated with cations. The final pH of equilibrium solution increased with increasing adsorbed P up to 689 mmol L⁻¹ of adsorbed P, but there was no further increase in final pH with additional P adsorption (Fig. 3). The final pH of equilibrium solution was 8.71 at 689 mmol L⁻¹ of adsorbed P. The pH of the soil solution increased as more OH⁻ was released into the soil solution through ligand exchange when specific P adsorption occurred. We assumed that the maximum amount of shared charge by sharing the P adsorption in the studied soil was 689 mmol L⁻¹ of adsorbed P. Phosphate removal from the above equilibrium solution might be attributed to P precipitation with calcium in alkaline pH conditions, instead of specific adsorption of P (Fig. 2).

The trend in the soil negative charge recorded after reacting with P was similar to that of the final pH of equilibrium solution (Fig. 4). The soil negative charge was 120 mmol c kg⁻¹ in the control, increased up to 164 mmol c kg⁻¹ at 689 mmol c kg⁻¹ of adsorbed P. This implies that total 44 mmol c kg⁻¹ of soil negative charge was increased by P adsorption. This increase in soil negative charge by P adsorption could be attributed to two reasons, first, the increase in pH-induced negative charge and second, the increase in P-induced negative charge. Phosphate adsorption could increase the pH-induced soil negative charge as OH⁻ was released from the edge of the crystals of clay minerals when specific adsorption of P occurred. Furthermore, the negative charge of the oxide group contained in P itself could contribute to the increase in soil negative charge. Each oxygen (O⁻²) in the orthophosphate (PO₄³⁻) has −0.75 of shared charge.

![Fig. 1 Cadmium solubility diagram with soil solution speciation by increasing K₂HPO₄ addition rate after 8 weeks of incubation at 25 °C. The CdCO₃ line assumes CO₂ (g) = 10⁻¹⁵ M](image)

![Fig. 2 Phosphate adsorption characteristics of the selected clay loam soil at 25 °C](image)
by sharing the charge with the \( P^{+5} \) atom. This “shared charge” is determined by dividing the valence of \( P \) by the number of bonded O atoms [26].

**Cadmium adsorption**

The pattern of Cd adsorption to P adsorbed soil was similar to that of the soil negative charge (Fig. 5). Cadmium adsorption was \( 139 \text{ mmol}_c \text{ kg}^{-1} \) in the control and increased up to \( 161 \text{ mmol}_c \text{ kg}^{-1} \) at \( 689 \text{ mmol}_c \text{ P kg}^{-1} \) of adsorbed P, implying that a total of \( 22 \text{ mmol}_c \text{ kg}^{-1} \) of Cd was adsorbed onto the negative site in the soil. The Cd maximal adsorption corresponded to maximal P adsorption \( (689 \text{ mmol}_c \text{ P kg}^{-1}) \), possibly implying that Cd possibly occupied all adsorption sites made by P adsorption, and that the maximum concentration of P adsorbed soil did not provide more Cd adsorption sites. However, the negative charge at P maximal adsorption \( (689 \text{ mmol}_c \text{ P kg}^{-1}) \) was \( 164 \text{ mmol}_c \text{ kg}^{-1} \) (Fig. 4) and was not the same as the Cd maximal adsorption \( (161 \text{ mmol}_c \text{ kg}^{-1}) \) (Fig. 5). Moreover, Cd adsorption did not have a significant correlation with P adsorption but showed a significantly positive correlation with soil negative charge \( (r=0.841^* \) (Table 3). Based on the above results, we assumed that Cd was not adsorbed to all adsorption sites created by adsorbed P.

**Contribution of pH-induced negative charge to Cd adsorption**

The soil negative charge with P adsorption was found to increase as both pH- and P-induced negative charges increased. The soil negative charge had a more significant positive correlation with the final pH \( (r=0.977^**) \) than with P adsorption \( (r=0.830^*) \) (Table 3), implying that changes in soil pH caused by P adsorption could explain changes in negative charge better than that of P adsorption itself. The soil negative charge used for the adsorption test increased significantly with increasing soil pH (in the range of pH 3.1–10.0; Fig. 6). The soil negative charge was \( 120 \text{ mmol}_c \text{ kg}^{-1} \) at pH 6.97 which was the initial pH of soil used for the adsorption test. This increased to \( 161 \text{ mmol}_c \text{ kg}^{-1} \) at pH 8.70, which was the soil pH at \( 689 \text{ mmol}_c \text{ kg}^{-1} \) of P adsorption. Therefore, \( 41 \text{ mmol}_c \text{ kg}^{-1} \) of the total increase in soil negative charge \( (44 \text{ mmol}_c \text{ kg}^{-1}) \) with \( 689 \text{ mmol}_c \text{ kg}^{-1} \) of P adsorption was caused by an increase in pH-induced negative charge and \( 3 \text{ mmol}_c \text{ kg}^{-1} \) of that was originated from an increase in P-induced negative charge. Therefore, contributions of the increase in pH-induced negative charge and P-induced negative charge to the total increase in soil negative charge with \( 689 \text{ mmol}_c \text{ kg}^{-1} \) of P adsorption were 93.2 and 6.8%, respectively.

Fig. 3 Final pH of equilibrium solution after phosphate adsorption

Fig. 4 Changes in soil negative charge due to increased phosphate adsorption to clay loam soil at 25°C

Fig. 5 Cd-adsorption to phosphate adsorbed soil after reacting with 500 mg Cd L\(^{-1}\) of CdCl\(_2\) solution at 25 °C
In conclusion, Cd might precipitate as $\text{Cd}_3(\text{PO}_4)_2$ under extremely high P addition ($16,000 \text{ mg P kg}^{-1}$). The formation of Cd minerals might not occur with P under the recommended field application rate of P fertilizer. Cd solubility might be controlled by another mechanism rather than precipitation under low P application systems. Phosphate adsorption increased the soil negative charge and Cd adsorption. Contributions of the increase in pH- and P-induced negative charges to the total increase in soil negative charge were 93.2 and 6.8%, respectively. The concurrent increase in Cd adsorption with P adsorption was mainly attributed to the increase in pH-induced negative charge.

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Authors’ contributions
CR and SUK carried out soil sampling, soil analyses, and data organization. COH participated in interpreting the obtained results and organizing the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials
Not applicable.

Table 3 Correlation coefficients between each parameter

| Parameter      | Cd adsorption | Final pH | Negative charge | P adsorption |
|----------------|---------------|----------|-----------------|--------------|
| Cd adsorption  | 1.000         | 0.934*** | 0.841***        | 0.599        |
| Final pH       | 1.000         |          | 0.977***        | 0.763*       |
| Negative charge| 1.000         |          | 0.830***        | 1.000        |

*, **, and *** represent significance at the 0.05, 0.01, and 0.001 levels, respectively.

Competing interests
The authors declare that they have no competing interests.

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References
1. Takijima Y, Katsumi F (1973) Cadmium contamination of soils and rice plants caused by zinc mining IV. Use of soil amendment materials for the control of Cd uptake by plants. Soil Sci Plant Nutr 19:235–244
2. Cao RL, Huo WR, He ZL, Hu AT, Deng BE (1993) Study on controlling cadmium pollution in paddy soil in Luo Quio township, Dayie county. China Envir Sci 3:433–439
3. Hong CO, Lee DK, Chung DY, Kim PJ (2007) Liming effects on cadmium stabilization in upland soil affected by gold mining activity. Arch Environ Contam Toxicol 52:496–502
4. Hong CO, Chung DY, Lee DK, Kim PJ (2010) Comparison of phosphate materials for immobilizing cadmium in soil. Arch Environ Contam Toxicol 58:268–274
5. Kim SU, Owens VN, Kim SY, Hong CO (2017) Effect of different way of bottom ash and compost application on phytoextractability of cadmium in contaminated arable soil. Appl Biol Chem 60:353–362
6. Lee HH, Heo DY, Han HR, Park YL, Ruangcharus C, Kim SU, Seo DC, Oh TK, Hong CO (2019) Evaluation of the effects of mandarin (Citrus reticulate) by-products containing citric acid on immobilization of cadmium in arable soils. Appl Biol Chem 62:45
7. Levi-Minzni R, Petruzelli G (1984) The influence of phosphate fertilizers on Cd solubility in soil. Water Air Soil Pollut 23:423–429
8. Naidu R, Bolan NS, Kookana RS, Tiller KG (1994) Ionic strength and pH effects on the adsorption of cadmium and the surface charge of soils. Eur J Soil Sci 45:419–429
9. Jeanjean J, Fedoroff M, Faverjon F, Vincent U, Corset J (1995) Influence of pH on the sorption of cadmium ions on calcium hydroxyapatite. J Mater Sci 30:5433–5439
10. Mandjiny S, Matis KA, Fedoroff M, Jeanjean J, Rouchaud JC, Toulhoat N, Potocki V, Maireles-Torres P, Jones D (1998) Calcium hydroxyapatites: evaluation of sorption properties for cadmium ions in aqueous solution. J Mater Sci 33:5433–5439
11. Hong CO, Owens VN, Kim YG, Lee SM, Park HC, Kim KK, Son HJ, Suh JM, Lee YB, Kim PJ (2014) Comparative effect of two different types of phosphate on cadmium uptake by radish (Raphanus sativa L) grown in arable soil affected by mine activity. Commun Soil Sci Plant Anal 45:1133–1148
12. Street JJ, Sabey BR, Lindsay WL (1978) Influence of pH, phosphorus, cadmium, sewage sludge and incubation time on the solubility and plant uptake of cadmium. J Environ Qual 7:286–290
13. Hong CO, Owens VN, Kim YG, Lee SM, Park HC, Kim KK, Son HJ, Suh JM, Kim PJ (2014) Soil pH effect on phosphate induced cadmium precipitation in arable soil. Bull Environ Contam Toxicol 93:101–105

Fig. 6 Changes in negative charge after adjusting pH of clay loam soil

Table 3 Correlation coefficients between each parameter

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*, **, and *** represent significance at the 0.05, 0.01, and 0.001 levels, respectively.

Fig. 6 Changes in negative charge after adjusting pH of clay loam soil

In conclusion, Cd might precipitate as $\text{Cd}_3(\text{PO}_4)_2$ under extremely high P addition ($16,000 \text{ mg P kg}^{-1}$). The formation of Cd minerals might not occur with P under the recommended field application rate of P fertilizer. Cd solubility might be controlled by another mechanism rather than precipitation under low P application systems. Phosphate adsorption increased the soil negative charge and Cd adsorption. Contributions of the increase in pH- and P-induced negative charges to the total increase in soil negative charge were 93.2 and 6.8%, respectively. The concurrent increase in Cd adsorption with P adsorption was mainly attributed to the increase in pH-induced negative charge.
14. Bolan NS, Adriano DC, Mani P, Duraisamy A, Arulmozhiselvan S (2003) Immobilization and phytoavailability of cadmium in variable charge soils. I. Effect of phosphate addition. Plant Soil 250:83–94
15. Wang B, Xie Z, Chen J, Jiang J, Su Q (2008) Effects of field application of phosphate fertilizers on the availability and uptake of lead, zinc and cadmium by cabbage (Brassica Chinensis L.) in a mining tailing contaminated soil. J Environ Sci 20:1109–1117
16. ME (2005) The Korean soil environmental conservation act. ME, Gwacheon
17. Allison LE (1965) Organic carbon. In: Black CA (ed) Methods of soil analysis. Part II, chemical and microbiological properties. American Society of Agronomy Inc Publishing, Madison, pp 1367–1376
18. RDA (1988) Methods of soil chemical analysis. National Institute of Agricultural Science and Technology RDA, Wanju
19. Schofield RK (1949) Effect of pH on electric charges carried by clay particles. J Soil Sci 1:1–8
20. Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. Anal Chem Acta 27:31–36
21. Lindsay WL (1979) Chemical equilibria in soils. Wiley, New York
22. Sparks DL (2003) Environmental soil chemistry. Academic Press, Newark
23. Santillan-Medrano J, Jurinak JJ (1975) The chemistry of lead and cadmium in soil: solid phase formation. Soil Sci Soc Am Proc 39:851–856
24. Street JJ, Lindsay WL, Sabey BR (1977) Solubility and plant uptake of cadmium in soils amended with cadmium and sewage sludge. J Environ Qual 6:72–77
25. RDA (1999) Recommendation standard of fertilization for crops. National Institute of Agricultural Science and Technology RDA, Wanju
26. McBride MB (1994) Environmental chemistry of soils. Oxford University Press, New York

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