Contrasting effect of phosphate on phytoavailability of arsenic and cadmium in soils supporting medicinal plants

Yong Dong Noh¹ · Hye Jin Park¹ · Kwon Rae Kim² · Won Il Kim³ · Ki Youl Jung⁴ · Sung Un Kim¹ · Vance N. Owens⁵ · Jin Seong Moon⁶ · Sung Wook Yun⁷ · Sang Yoon Kim⁸ · Chang Oh Hong¹

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Abstract Soil and plant samples were collected from 84 fields where medicinal plants were cultivated to determine the effect of soil phosphate (P) on the concentration of plant-available arsenic (As) and cadmium (Cd) and on the uptake of these toxic elements by medicinal plants. Concentrations of total P and available P in soils affected the phytoavailability of As and Cd differentially. Plant-available As in the soil and its uptake in the plant increased with increasing concentration of plant-available P in the soil due to competition between arsenate and P for the adsorption site at the soil surface and an increase in soil pH caused by specific adsorption of P. In contrast, phytoavailability of Cd decreased with increasing concentration of available P in soil. This was mainly attributed to an increase in Cd adsorption caused by P-induced negative charge of soil.

Keywords Adsorption · Arsenic · Cadmium · Phosphate fertilizer · Plant availability

Introduction

Recently, there has been an increasing demand for medicinal plants to be used as raw materials in the pharmaceutical industries and as dietary supplements [1]. However, several studies have reported illness and fatalities resulting from the intake of these complementary medicines [2–4]. Poisonings associated with the presence of toxic elements in medicinal plants were reported in Asia, Africa, Europe, and the USA [5–10]. Arsenic (As) and Cadmium (Cd) can be particularly toxic to humans. Arsenic can cause chronic lung disease, chronic liver disease, polyneuropathy, peripheral vascular disease, hypertension, ischemic heart disease, diabetes mellitus, non-pitting edema of feet/hands, weakness, and anemia [11]. Itai-itai disease (“it hurts-it hurts disease”) is caused by Cd poisoning [12], and chronic exposure to Cd can cause nephrotoxicity in humans, mainly due to abnormalities in tubular re-absorption [13].

Plants may contain toxic elements when these elements are present in the soil [14, 15]. Several studies reported that concentration of As and Cd in plant tissue was significantly related to the concentration of the plant-available forms of these elements in soil [16–19]. Concentrations of plant-
available As and Cd are easily influenced by chemical properties of soil such as pH, cation exchange capacity, organic matter, and phosphate (P) concentration [20, 21]. In particular, P addition could significantly affect the concentration of plant-available As due to their similar chemical forms (e.g., arsenate [AsO$_4^{3-}$] and P [PO$_4^{3-}$]) in soil. These oxyanions compete for adsorption sites at the surface of soil colloids [22]. Therefore, arsenate solubility in arable soils could be influenced by the application of P fertilizer. Also, Cd solubility could be affected by the presence of P in soil because of precipitation of Cd in various P-associated Cd minerals [23, 24]. Phosphate fertilizer was reported to be effective inorganic amendment to reduce the phytoavailability of Cd in arable soils [25–27]. However, P fertilizers may also be a source of some of these metal(loid)s including Cd [28, 29].

Phosphorous is one of the macronutrients for growth and reproduction of all plants including medicinal plants ([30]; Marschner et al. 2012). It is necessary to apply P fertilizer to the soil in order to support the complete growth of medicinal plants. Usually, considerable amount of P fertilizer (60–120 kg P$_2$O$_5$/ha) is annually applied to the soil supporting medicinal plant cultivation in Korea. As mentioned above, P addition could affect bioavailability of As and Cd in soil. Therefore, this study was conducted to determine the effect of P addition on plant-available concentrations of As and Cd in soil, and the subsequent uptake of these toxic elements by medicinal plants.

Materials and methods

Sampling and preparation

The sampling locations for this study are shown in Fig. 1. Soil and plant samples were collected from 84 fields in 6 provinces (Chungbuk, Chungnam, Gyeongbuk, Gyeongnam, Gangwon, and Jeonnam) of Korea. These provinces are the important bases for cultivating medicinal plants in Korea. These areas have a type of monsoon climate with four distinct seasons. Winter is usually long, cold, and dry, whereas summer is short, hot, and humid. Spring and autumn are pleasant but short in duration. These areas have sufficient rainfall to sustain their agriculture. Rarely does less than 750 mm of rain fall in any given year; for the most part, rainfall is over 1000 mm. Mean temperature in January ranges from $-5$ to $-2.5^\circ$C; in July, the mean temperature is about $22.5$–$25^\circ$C. The target medicinal fields are mainly located on mountainous territory with high elevations. The slopes are steeper, and elevation of these fields ranges from 462 to 1152 m. Thus, these areas meet the growth requirements for many Korea medicinal plants.

Fig. 1 Map of locations where samples of soil and medicinal plants were collected in Korea (A) Hoengseong and Hongcheon in Gangwon Province, (B) Jecheon and Goesan in Chungbuk Province, (C) Andong and Bonghwa in Gyeongbuk Province, (D) Geumsan in Chungnam Province, (E) Sacheon, Haman, Sancheong, Jinju, Uiryeong in Gyeongnam Province, (F) Miryang in Gyeongnam Province, (G) Jangheung, Naju, Goheung, Yeongam in Jeonnam Province)
Six species of medicinal plants (*Angelica gigas*, *Astragalus membranaceus*, Atractylodes macrocephala Koidzumi, *Codonopsis lanceolata*, *Platycodon grandiflorum*, and *Rehmannia glutinosa*) were included in the sampling process. Medicinal plants grown for 1 year and same size of plant within each species were collected from the fields. Soil and plant samples were collected from September 1 to October 30, 2013. Three surface soil samples were collected using a hand auger (5 cm diameter and 15 cm depth) from random areas in each field. These three soil samples were composited for chemical analysis. Soil samples were air-dried and ground to pass a 2-mm screen in preparation for chemical analysis.

Plant samples were collected from three random spots in each field and separated into roots and shoots. Only roots were analyzed for As and Cd since this is the only plant part used for medicinal purposes in all species evaluated. Roots were brushed to remove soil residue, washed with distilled water, and oven-dried at 105 °C for 48 h. Dried root samples were ground to a fine powder using an electric blender and then stored in airtight tubes pending chemical characterization.

### Incubation experiment

To confirm the effect of P on extractability of As and Cd in soil, an upland soil located nearby the Bongsan gold mine area in Hapcheon Council, Gyeongnam Province, South Korea (128°010N and 34°370E), which was contaminated with As (26.3 mg/kg) and Cd (9.1 mg/kg), was selected for the incubation experiment. The soil of target area was collected, dried, ground through a 2-mm sieve, and stored in the plastic container before incubation experiment. Five hundred gm soils was mixed at the different rates of K₂HPO₄ (0, 200, 400, 800, and 1600 mg P/kg) in plastic beakers, incubated in a growth chamber at 25 °C for 8 weeks, and moistened with 70% of the soil pore volume by periodically weighing the beakers and adjusting the weight by adding distilled water. Experiment was conducted in triplicate, and plastic beakers were randomly placed in incubator.

### Chemical analysis

The sieved soils (<2 mm) were analyzed for pH (1:5 water suspension). The available P content was determined using the Lancaster method [31]. Total P was determined spectrophotometrically (470 nm) after digesting soil samples with perchloric acid. To determine plant-available As and Cd concentration (Symeonides and McRae 1977), dried soil samples were extracted with 1 M NH₄OAc (pH 7.0) at a soil:solution ratio of 1:10 for 1 h. Two gm of soils was digested with aqua regia, and digested solution was placed in 50-mL volumetric flask and then diluted to the mark with water for the measurement of total As and Cd concentration. Zero point two gm of the finely powdered plant roots was digested with a mixed solution (HNO₃:H₂SO₄: -HClO₄, 10:1:4 v/v), and digested solution was placed in 25-mL volumetric flask and then diluted to the mark with water for As and Cd analyses.

### Analytical accuracy

Extracted As and Cd solutions were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS, Thermo Scientific iCAP Q, Bremen, Germany). To qualify analysis method for total As and Cd concentration, BAM-U112a and SRM 1573a, certified reference materials, were analyzed using the above methods. Observed values for total As and Cd concentrations were above 90% of the values of the certified reference materials (Table 1). Heavy metal(loid)s in the solutions were quantified by ICP-MS. This ICP-MS maintained a very high accuracy, with detection limits of <0.022 and 0.00014 µg/L for As and Cd, respectively, and 0.013 µg/L for soil blank extracts, and 0.2 µg/L for blank digest solutions.

### Statistics

Statistical analysis was performed using SAS version 9.4 [32]. One M NH₄OAc extractable As and Cd concentrations in soils was used as indices of plant-available concentrations of these metal(loid)s. The data were subjected

### Table 1 Results of certified reference materials for checking the analytical accuracy

| Target sample | Reference material | Heavy metal | Analysis method | Certified value Mean ± Uᵃ (mg/kg) | Observed value (n = 3) AM ± SDᵇ (mg/kg) | Recovery rate AM ± SD (%) |
|---------------|-------------------|-------------|----------------|----------------------------------|----------------------------------------|---------------------------|
| Soil          | BAM-U112a         | As          | Total          | 10.3 ± 0.5                       | 9.8 ± 0.15                             | 95.1 ± 1.48                |
|               |                   | Cd          | Total          | 4.12 ± 0.15                     | 4.3 ± 0.06                             | 104.4 ± 1.40              |
| Plant         | SRM 1573a         | As          | Total          | 0.112 ± 0.004                   | 0.106 ± 0.004                         | 95 ± 0.5                  |
|               |                   | Cd          | Total          | 1.52 ± 0.08                     | 1.42 ± 0.03                           | 93 ± 2.0                  |

ᵃ U uncertainty (half-width of the 95% confidence interval)
ᵇ AM ± SD arithmetic mean ± standard deviation
to correlation analysis using PROC CORR to identify associations between (1) total P concentration and total As and Cd concentrations in soils, (2) available P and available As and Cd concentration in soils, (3) available P concentration and As and Cd concentration in medicinal plants. Comparison of means was calculated using Tukey’s studentized range (HSD) test for the traits with a significant difference ($p = 0.05$) among medicinal plants. Data analysis including ANOVA and mean separation was performed in Statistix 9 [33]. Least significance differences were used to separate means when $F$ tests were statistically significant ($p = 0.05$).

Results and discussion

Total soil As and Cd

To determine the relationships between P concentration and concentrations of As and Cd in soils supporting for medicinal plants, total concentrations of P, As, and Cd were measured. There was a significant negative correlation between total soil P and total soil As ($r = 0.378$, $p < 0.001$) and a significant positive correlation between total soil P and total soil Cd ($r = 0.382$, $p < 0.001$) (Fig. 2). Total concentrations of As and Cd in soils collected from 84 medicinal plant fields ranged from 0.11 to 10.5 mg/kg and from 0.003 to 0.21 mg/kg, respectively. These concentrations did not exceed safety levels (25 mg/kg for As and 4 mg/kg for Cd) established by the Korean Soil Environmental Conservation Act. Total soil P concentration across the 84 sites ranged from 211 to 2647 mg/kg.

The concentration of total As in the soil decreased as total soil P increased (Fig. 2A). Arsenate and P are chemically similar; both are typically present as oxyanions in the soil. The most probable oxidation states of As in soil environments are +3 and +5. Arsenite (+3) is the reduced state from As (+5) that is most likely to be found in anaerobic soils. Arsenate (+5), AsO$_4^{2-}$, the oxidized state, is stable in aerobic soils [34]. Soils used in this study were usually managed in oxidative conditions throughout the year. Therefore, most of the As is likely to exist in the oxidized (arsenate) form in these soils. Furthermore, other work demonstrated that arsenite is rapidly oxidized to arsenate after contact with soil under aerobic conditions [35]. Phosphate ions in the soil may increase arsenate mobility by competing for adsorption sites on the soil surface, because the chemical behavior of arsenate is similar to that of P (PO$_4^{3-}$) in soils. When mobile in the soil, arsenate can be taken up by medicinal plants such as those evaluated in this study, or it can be easily lost through leaching [36]. A high concentration of total P might accelerate loss of As from surface soil by leaching.

The concentration of total Cd in the soil increased as total soil P increased (Fig. 2B). The principle reason for an increase in total soil Cd with the increasing concentration of total P is the source of P fertilizers used on agricultural soils. Three main types of commercial phosphate fertilizer (fused phosphate, fused superphosphate, and superphosphate) are utilized on farms in Korea. These phosphate fertilizers contain Cd, ranging from 2.1 to 3.4 mg Cd/kg. Thus, long-term application of these types of phosphate fertilizer could result in accumulation of Cd in arable soil. The phosphate fertilizers have been consecutively applied in the studied medicinal fields for more than 11 years.

![Fig. 2](image-url)  
**Fig. 2** Relationship between total soil P concentration and total concentration of As (A) and Cd (B) in soils supporting for medicinal plants ($p < 0.001$, $p < 0.01$, and $p < 0.05$ denoted by ***, **, and *, respectively)
McGrath and Tunney [29] reported that phosphate fertilizer application for 31 consecutive years increased Cd concentration in arable soils in Ireland.

Plant-available As and Cd

To determine the relationships between plant-available P concentration and concentrations of plant-available As and Cd, plant-available P was measured using Lancaster extraction method and plant-available As and Cd was analyzed using 1 M NH₄OAc extraction method. In contrast to the relationship between total soil P concentration and total soil As and Cd concentrations, while the concentration of 1 M NH₄OAc extractable As in soil was positively related to the plant-available P concentration, the concentration of 1 M NH₄OAc extractable Cd was negatively related (Fig. 3A, B).

The increase in the concentration of 1 M NH₄OAc extractable As in soils with increasing plant-available P is likely related to two factors. First, arsenate and P may be competing for adsorption site on the surface of soil particles as mentioned above. In a laboratory experiment, Pereyra [37] reported that arsenate release from soil was positively related to increased P concentration. Second, there is an increase in soil pH due to P adsorption. Like P, arsenate bioavailability may be high in neutral pH conditions. Arsenate adsorbs on surface of clay and iron oxide most effectively at low pH; consequently, its mobility is fairly low in acidic soils with high clay or oxide content. In calcareous soils, it adsorbs to calcite or forms calcium arsenate precipitates [34]. Specific adsorption of P to surface of soil colloids results in release of OH⁻ groups and a concomitant increase in soil pH. Soil pH was significantly related to plant-available P ($r = 0.331$, $p < 0.01$) (Fig. 4).

Using linear equation, soil pH increased from 5.89 at 0 mg P/kg of plant-available phosphorus to near-neutral pH (7.12) at 358 mg P/kg of available P. The decrease in the concentration of 1 M NH₄OAc extractable Cd in soils with increasing plant-available P is partly due to an increase in Cd adsorption to the surface of soil colloids. As mentioned above, specific adsorption of P to clay particles increases the soil pH by releasing OH⁻ groups, a phenomenon that increases with P fertilization. Several studies have reported that Cd²⁺ adsorption increased in elevated pH condition [17, 25], causing decrease in phytoavailability of Cd. Changing soil pH directly affects the negative charge of soil and Cd extractability. Cd²⁺ is likely to adsorb to negatively charged soil surfaces, thus reducing its extractability. Addition of P-induced change in soil pH and subsequently affected the extractability of Cd in soils [38]. Hong et al. [17] reported that decrease in Cd extractability with addition of P could be attributed mainly to Cd adsorption resulting from increases in soil pH and negative charge.

Plant uptake of As and Cd

To examine how P concentration in soil affects uptake of As and Cd in medicinal plants, plant arable P concentration in soil was measured using Lancaster extraction method and concentration of As and Cd in plants was analyzed using digestion by the ternary solution. While As concentration in medicinal plants was positively related ($r = 0.291$, $p < 0.01$) to plant-available P in the soil, Cd concentration was negatively related ($r = 0.400$, $p < 0.001$) (Fig. 5A, B). Cao et al. [39] reported that P

![Fig. 3](image-url) Relationships between plant-available P concentration and the concentration of 1 M NH₄OAc extractable As (A) and Cd (B) in soils supporting for medicinal plants ($p < 0.001$, $p < 0.01$, and $p < 0.05$ denoted by ***, **, and *, respectively)
amendment increased the effectiveness of Chinese brake fern to remediate As-contaminated soils, by increasing As uptake. Even though they used As hyperaccumulator plant for the study, their result evidenced that plant could take up more As in soils with high P level compared with low P level. Several studies reported that Cd uptake by agricultural crops decreased with increasing P application rate in Cd-contaminated soil [23, 40]. These reports also evidenced our results in this study.

The relationship between the concentration of plant-available P in soil and concentration of As and Cd taken up by medicinal plants was similar to that between plant-available P and 1 M NH4OAc extractable As and Cd in the soil. Other studies have also reported a similar relationship between heavy metals in the soil and subsequent uptake in the plant [17, 41, 42].

Linear regression analysis was applied in this study to find the effect of available P concentration in soil on As and Cd uptake by each medicinal plant. The results of this analysis are summarized in Table 2. Available P concentration in soil was related positively with As concentrations in medicinal plants on Angelica gigas, Codonopsis lanceolate, Platycodon grandiflorum, and Rehmannia glutinosa; by contrast, it was related negatively with Cd concentrations on Astragalus membranaceus, Codonopsis lanceolate, and Rehmannia glutinosa.

Concentrations of As and Cd in six species of medicinal plant ranged from 0.006 to 4.31 mg/kg and from 0.021 to

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**Fig. 4** Relationship between plant-available P and soil pH in soils supporting for medicinal plants (p < 0.001, p < 0.01, and p < 0.05 denoted by ***, **, and *, respectively)

**Fig. 5** Relationship between plant-available P concentration in the soil and As concentration (A) and Cd concentration (B) in medicinal plants (p < 0.001, p < 0.01, and p < 0.05 denoted by ***, **, and *, respectively)
Of all medicinal plants collected from 84 target fields, 1.2 and 21.4% medicinal plants exceeded safety levels for As (3 mg/kg) and for Cd (0.3 mg/kg) established by the Korean Ministry of Food and Drug Safety (Table 3). While mean values of As concentration in each medicinal plant did not exceed safety level for As, one of 12 angelica gigas plants exceeded. Mean values of As concentrations in Astragalus membranaceus, Atractylodes macrocephala Koidzumi, and Rehmannia glutinosa were significantly higher than those

| Plant species                  | n  | Regression equation                        | $R^2$  |
|-------------------------------|----|--------------------------------------------|--------|
| Angelica gigas               | 12 | Plant As = $-1.910 + 0.022 \times \text{Av. P}$ | 0.533**d |
|                              |    | Plant Cd = $0.362 – 7.839 \times 10^{-4} \text{ Av. P}$ | 0.297  |
| Astragalus membranaceus      | 11 | Plant As = $0.168 + 5.676 \times 10^{-3} \text{ Av. P}$ | 0.276  |
|                              |    | Plant Cd = $0.244 – 4.556 \times 10^{-4} \text{ Av. P}$ | 0.441* |
| Atractylodes macrocephala Koidzumi | 14 | Plant As = $0.217 + 4.279 \times 10^{-3} \text{ Av. P}$ | 0.164  |
| Codonopsis lanceolata        | 14 | Plant As = $0.015 + 6.501 \times 10^{-4} \text{ Av. P}$ | 0.286* |
|                              |    | Plant Cd = $0.343 – 3.604 \times 10^{-4} \text{ Av. P}$ | 0.430* |
| Platycodon grandiflorum      | 18 | Plant As = $0.024 + 3.855 \times 10^{-4} \text{ Av. P}$ | 0.270* |
|                              |    | Plant Cd = $0.317 – 3.325 \times 10^{-4} \text{ Av. P}$ | 0.117  |
| Rehmannia glutinosa          | 15 | Plant As = $0.648 + 5.911 \times 10^{-3} \text{ Av. P}$ | 0.307* |
|                              |    | Plant Cd = $0.324 – 1.124 \times 10^{-3} \text{ Av. P}$ | 0.415**|

- **Plant As** = Arsenic concentration in each medicinal plant
- **Plant Cd** = Cadmium concentration in each medicinal plant
- **Av. P** = Available phosphorus concentration in soil
- $p < 0.01$ and $p < 0.05$ denoted by ** and *, respectively

0.57 mg/kg, respectively. Of all medicinal plants collected from 84 target fields, 1.2 and 21.4% medicinal plants exceeded safety levels for As (3 mg/kg) and for Cd (0.3 mg/kg) established by the Korean Ministry of Food and Drug Safety (Table 3). While mean values of As concentration in each medicinal plant did not exceed safety level for As, one of 12 angelica gigas plants exceeded. Mean values of As concentrations in Astragalus membranaceus, Atractylodes macrocephala Koidzumi, and Rehmannia glutinosa were significantly higher than those

### Table 3: As and Cd concentrations and bioconcentration factors of medicinal plant species

| Plant species                  | n  | Heavy metal in medicinal plant (mg/kg) | Bioconcentration factora |
|-------------------------------|----|--------------------------------------|--------------------------|
|                              |    | As                                  | Cd                       |
| Angelica gigas               | 12 | Max 4.31                             | 0.39                     | 21.3 | 18.6 |
|                              |    | Min 0.01                             | 0.06                     | 0.05 | 1.26 |
|                              |    | Mean 0.88ab                          | 0.24ab                   | 2.60b| 8.62b|
| Astragalus membranaceus      | 11 | Max 2.77                             | 0.17                     | 3.27 | 8.12 |
|                              |    | Min 0.14                             | 0.13                     | 0.12 | 0.75 |
|                              |    | Mean 1.48a                           | 0.16b                    | 0.96b| 2.78b|
| Atractylodes macrocephala Koidzumi | 14 | Max 2.62                             | 0.40                     | 2.78 | 21.7 |
|                              |    | Min 0.02                             | 0.04                     | 0.02 | 0.42 |
|                              |    | Mean 1.38a                           | 0.21b                    | 0.78b| 7.20b|
| Codonopsis lanceolata        | 14 | Max 0.59                             | 0.33                     | 0.17 | 8.37 |
|                              |    | Min 0.01                             | 0.02                     | 0.009| 4.75 |
|                              |    | Mean 0.14bc                          | 0.22b                    | 0.074b| 5.73ab|
| Platycodon grandiflorum      | 18 | Max 0.21                             | 0.57                     | 0.077| 9.49 |
|                              |    | Min 0.01                             | 0.21                     | 0.002| 4.06 |
|                              |    | Mean 0.08c                           | 0.34*                    | 0.029b| 6.97ab|
| Rehmannia glutinosa          | 15 | Max 2.42                             | 0.38                     | 13.0 | 17.5 |
|                              |    | Min 0.02                             | 0.03                     | 0.002| 1.14 |
|                              |    | Mean 1.38a                           | 0.17b                    | 3.22a | 11.1a |
| Permissible safety levelb    | 3  | 0.3                                  |                          |

- a Ratio of heavy metal concentration in medicinal plant to that in the soil
- b Maximum permissible safety level for medicinal plants established by Ministry of Food and Drug Safety of Korea
in *Codonopsis lanceolata* and *Platycodon grandiflorum*. Mean value of Cd concentration in *Platycodon grandiflorum* exceeded safety level for Cd and more than one plant sample exceeding safety level for Cd was found in all medicinal plant species except for *Astragalus membranaceus*. In contrast to the As and Cd concentrations in medicinal plants, there were no total As and Cd concentrations in soils exceeding safety levels (25 mg/kg for As and 4 mg/kg for Cd) established by the Korean Soil Environmental Conservation Act. As shown in Table 2. As bioconcentration factor for *Rehmannia glutinosa* was significantly higher than that for *Codonopsis lanceolata* and *Platycodon grandiflorum*. Mean values of Cd bioconcentration factor for all medicinal plant species were higher than 1. This implies that all of studied medicinal plants could take up large amount of Cd from the soil despite low level of Cd in soil. High amounts of Cd accumulated in medicinal plants may be detrimental to human health. Therefore, attention should be paid to the effects of high accumulations of Cd in medicinal plants on human health.

**Effect of P on extractability of As and Cd**

To confirm the effect of P on extractability of As and Cd, 1 M NH₄OAc extractable As and Cd concentrations and chemical properties of soil were measured after incubation experiment. Changes in extractable As and Cd concentrations were contrast with increasing P addition rate (Fig. 6A). One M NH₄OAc extractable As and available P concentrations significantly increased with increasing P addition rate (Fig. 1A, B). The chemical behavior of arsenate is similar to that of phosphate (PO₄³⁻) in soils; it is chemisorbed by Fe and Al oxides, non-crystalline aluminosilicates, and to a smaller extent by layer silicate clays. Being the anion of the weak acid H₃AsO₄, with pKa values (2.24, 6.94, and 11.5) similar to those of phosphoric acid, arsenate adsorbs to sites on the soil surface most effectively at low pH [34]. As mentioned above, P ions in the soil may increase arsenate mobility by competing for adsorption sites on the soil surface. In addition, soil pH increased from 5.19 in control to 7.03 (near-neutral pH condition) at the

![Fig. 6](https://example.com/fig6.png) Changes in 1 M NH₄OAc extractable As and Cd concentrations (A), available P concentration (B), pH (C), negative charge (D) of soil added with different rates of K₂HPO₄ after 8 weeks of incubation at 25 °C

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rate of 1600 mg P kg\(^{-1}\) (Fig. 6C). This result confirmed the positive relationship between plant-available As and P in soils supporting medicinal plants (Fig. 3A).

In contrast to the change in 1 M NH\(_2\)OAc extractable As with P addition, 1 M NH\(_2\)OAc extractable Cd concentration significantly decreased with increasing P addition rate (Fig. 6A). This result also confirmed the negative relationship between plant-available Cd and P in soils supporting medicinal plants (Fig. 3B). As mentioned above, this might result from increase in negative charge-induced Cd adsorption to surface of soil colloids (Fig. 6D).

Results of field survey experiment and incubation experiment clearly demonstrated that the concentration of P in soils supporting medicinal plant growth contrastively affected distribution of As and Cd in soils and plants. Total As concentration in soil decreased with increasing concentration of total P due to leaching of As from the top soil, while total Cd concentration in soil increased as a result of the use of P fertilizers containing Cd. Plant-available As in the soil and its uptake in the plant increased with increasing concentration of plant-available P in the soil due to competition between arsenate and P for the adsorption site at the soil surface and an increase in soil pH caused by specific adsorption of P. In contrast, phytoavailability of Cd increased with increasing concentration of available P in soil. This might result from an increase in Cd adsorption caused by P-induced negative charge of soil.

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