Appl Biol Chem (2017) 60(2):119–128
DOI 10.1007/s13765-017-0262-3

Online ISSN 2468-0842
Print ISSN 2468-0834

ARTICLE

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

Yong Dong Noh[1] · Hye Jin Park[1] · Kwon Rae Kim[2] · Won Il Kim[3] · Ki Youl Jung[4] · Sung Un Kim[1] · Vance N. Owens[5] · Jin Seong Moon[6] · Sung Wook Yun[7] · Sang Yoon Kim[8] · Chang Oh Hong[1]

Received: 30 December 2016 / Accepted: 22 February 2017 / Published online: 3 March 2017

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

Yong Dong Noh and Hye Jin Park have contributed equally to this work.

✉ Chang Oh Hong
soilchem@pusan.ac.kr

[1] Department of Life Science and Environmental Biochemistry, Pusan National University, Miryang 50463, Republic of Korea

[2] Department of Agronomy and Medicinal Plant Resources, GNTECH, Jinju 660-758, Republic of Korea

[3] Chemical Safety Division, National Academy of Agricultural Science, Jeonju 560-500, Republic of Korea

[4] Coarse Cereal Crop Research Division, NICS, RDA, Miryang 627-830, Republic of Korea

[5] Plant Science Department and North Central Sun Grant Center, South Dakota State University, 1110 Rotunda Lane North, Brookings, SD 57007, USA

[6] Gyeongnam Agricultural Research & Extension Services, Onion Research Institute, Changnyeong 635-821, Republic of Korea

[7] Department of Agricultural Engineering, National Academy of Agricultural Science, RDA, Wanju, Jeonbuk 54875, Republic of Korea

[8] National Academy of Agricultural Science, Wanju-Gun 55365, Republic of Korea

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_2O_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 °C; in July, the mean temperature is about 22.5–25 °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.

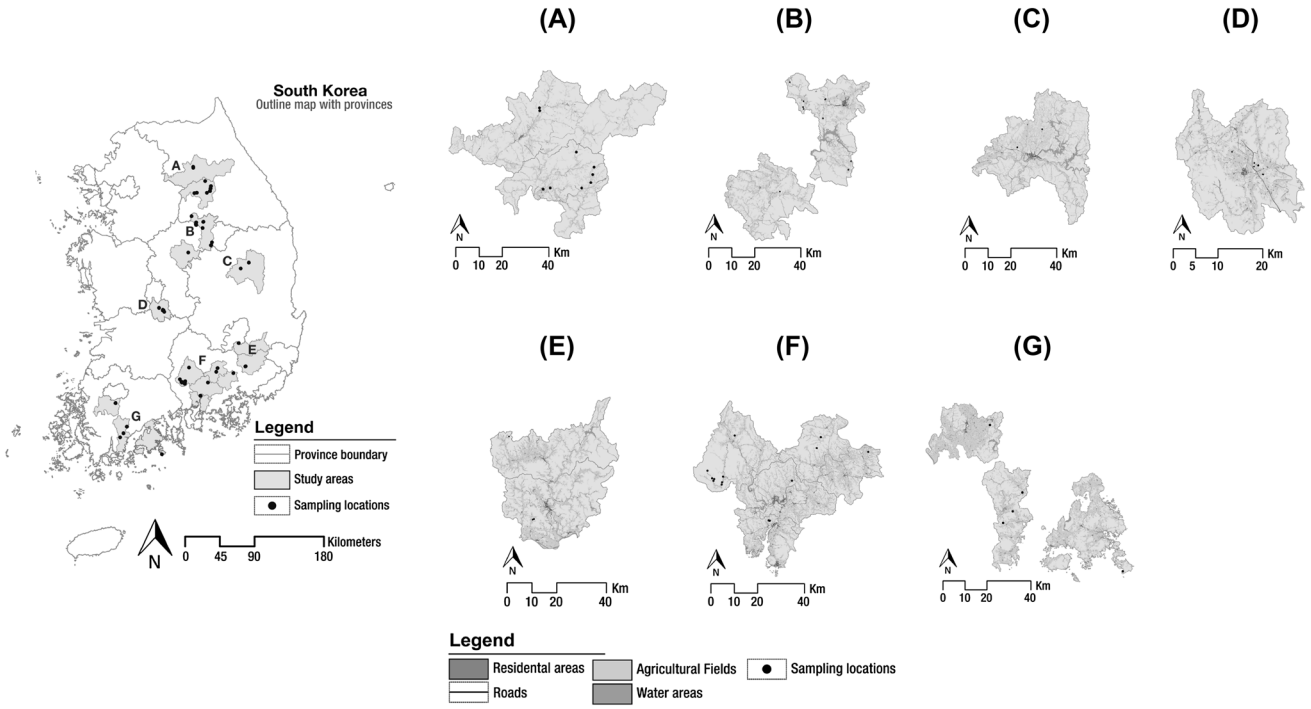

Fig. 1 Map of locations where samples of soil and medicinal plants were collected in Korea (**A**) *Hoengseong* and *Hongcheon* in *Gangwon* Province, (**B**) *Jecheon* and *Goesan* in *Chungbuk* Province, (**C**) *Andong* and *Bonghwa* in *Gyeongbuk* Province, (**D**) *Geumsan* in *Chungnam* Province, (**F**) *Sacheon*, *Haman*, *Sancheong*, *Jinju*, *Uiryeong* in *Gyeongnam* Province, (**E**) *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 K_2HPO_4 (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 NH_4OAc (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 (HNO_3:H_2SO_4:-$HClO_4$, 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 NH_4OAc 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 ± U[a] (mg/kg)	Observed value ($n = 3$) AM ± SD[b] (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^{3-}, 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.

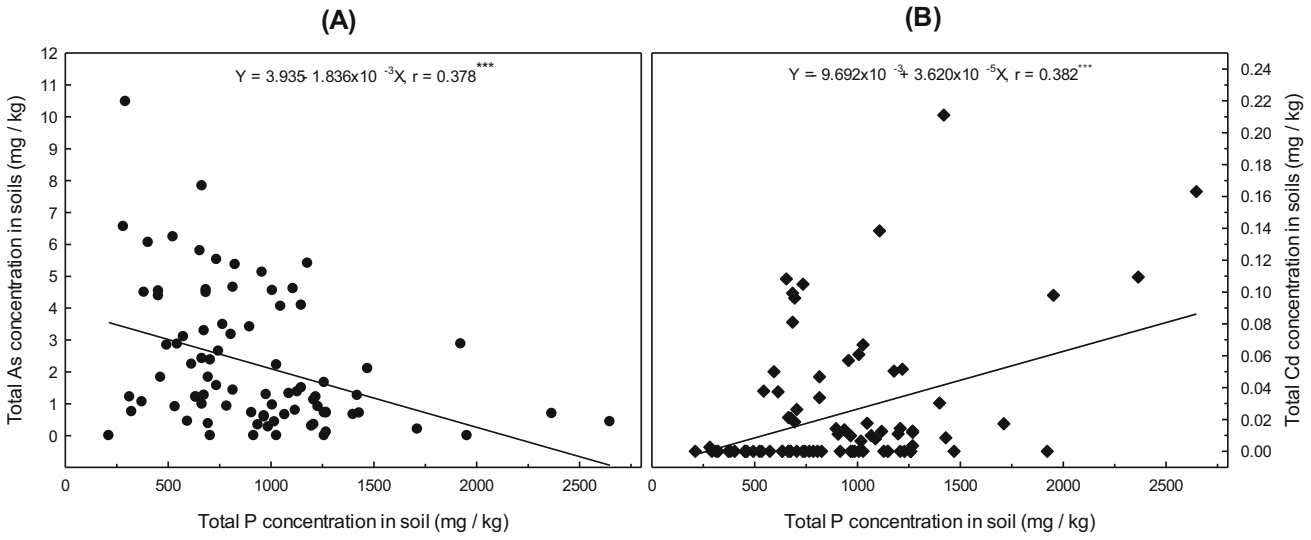

Fig. 2 Relationship between total soil P concentration and total concentration of As (**A**) and Cd (**B**) in soils supporting for medicinal plants ($p < 0.001$, $p < 0.01$, and $p < 0.05$ denoted by ***, **, and *, respectively)

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 NH_4OAc 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 NH_4OAc extractable As in soil was positively related to the plant-available P concentration, the concentration of 1 M NH_4OAc extractable Cd was negatively related (Fig. 3A, B).

The increase in the concentration of 1 M NH_4OAc 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, Peryea [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 NH_4OAc 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 Cd^{2+} 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. Cd^{2+} 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

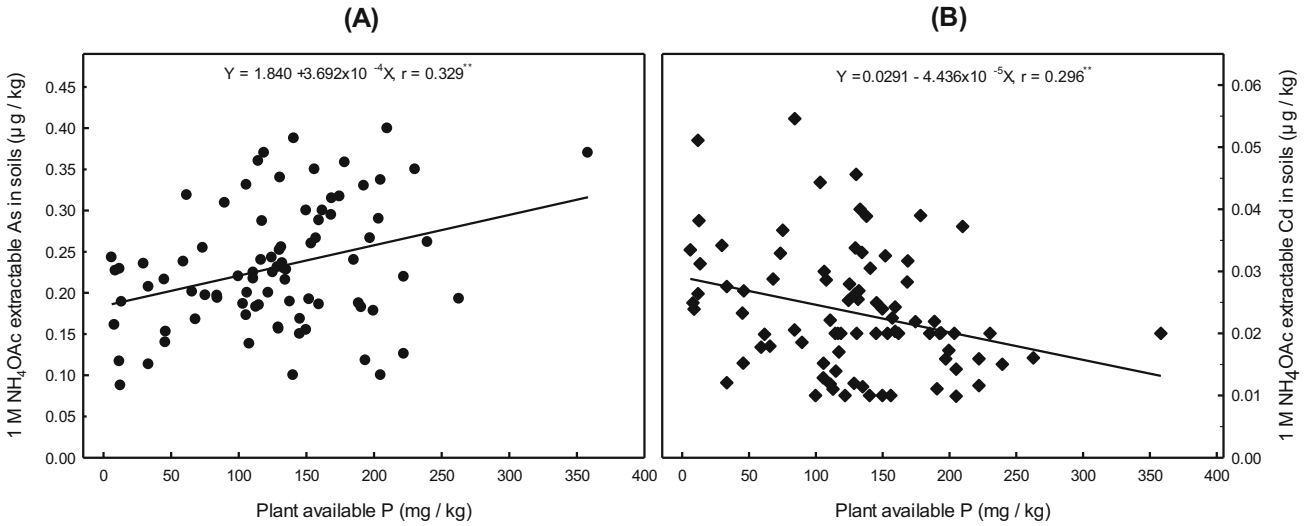

Fig. 3 Relationships between plant-available P concentration and the concentration of 1 M NH_4OAc extractable As (**A**) and Cd (**B**) in soils supporting for medicinal plants ($p < 0.001$, $p < 0.01$, and $p < 0.05$ denoted by ***, **, and *, respectively)

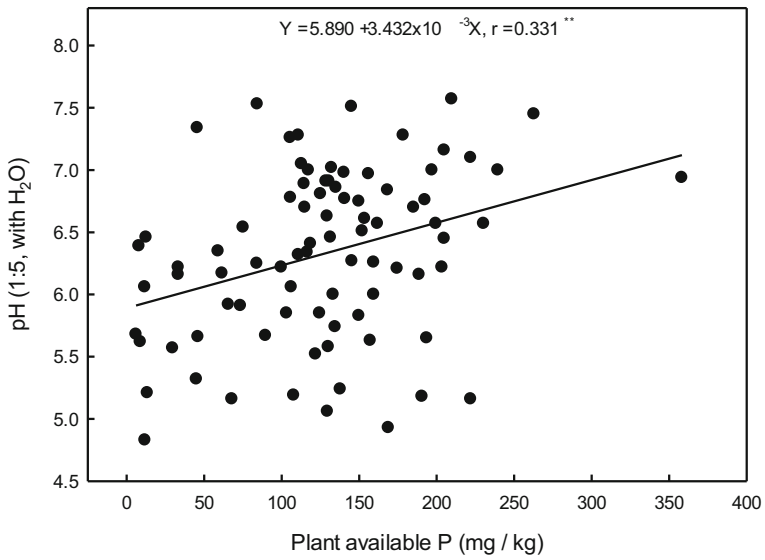

Fig. 4 Relationship between plant-available P and soil pH in soils supporting for medicinal plants ($p < 0.001$, $p < 0.01$, and $p < 0.05$ denoted by ***, **, and *, respectively)

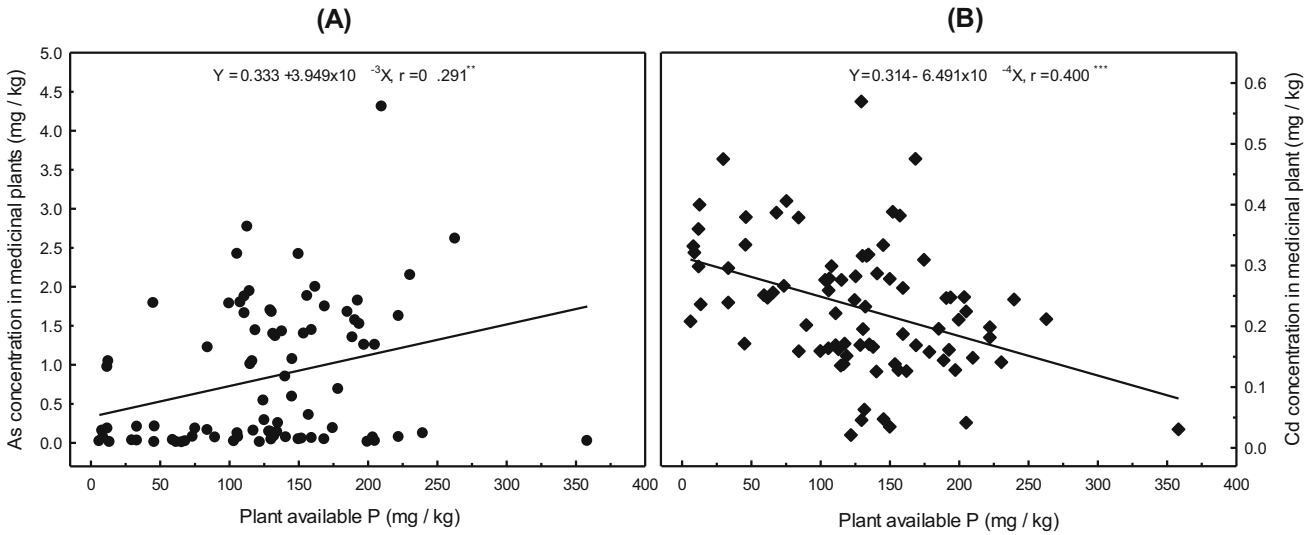

Fig. 5 Relationship between plant-available P concentration in the soil and As concentration (**A**) and Cd concentration (**B**) in medicinal plants ($p < 0.001$, $p < 0.01$, and $p < 0.05$ denoted by ***, **, and *, respectively)

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 NH_4OAc 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 gutinosa*.

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

Table 2 Linear regression equations for the estimation of As and Cd concentrations in each medicinal plant derived from available P concentration in soils

Plant species	*n*	Regression equation	R^2
Angelica gigas	12	Plant As[a] = −1.910 + 0.022 × Av. P[c]	0.533**[d]
		Plant Cd[b] = 0.362 – 7.839 × 10^{-4} Av. P	0.297
Astragalus membranaceus	11	Plant As = 0.168 + 5.676 × 10^{-3} Av. P	0.276
		Plant Cd = 0.244 – 4.556 × 10^{-4} Av. P	0.441*
Atractylodes macrocephala Koidzumi	14	Plant As = 0.217 + 4.279 × 10^{-3} Av. P	0.164
		Plant Cd = 0.258 – 3.709 × 10^{-4} Av. P	0.199
Codonopsis lanceolata	14	Plant As = 0.015 + 6.501 × 10^{-4} Av. P	0.286*
		Plant Cd = 0.343 – 3.604 × 10^{-4} Av. P	0.430*
Platycodon grandiflorum	18	Plant As = 0.024 + 3.855 × 10^{-4} Av. P	0.270*
		Plant Cd = 0.317 – 3.325 × 10^{-4} Av. P	0.117
Rehmannia glutinosa	15	Plant As = 0.648 + 5.911 × 10^{-3} Av. P	0.307*
		Plant Cd = 0.324 – 1.124 × 10^{-3} Av. P	0.415**

[a] Plant As = Arsenic concentration in each medicinal plant

[b] Plant Cd = Cadmium concentration in each medicinal plant

[c] Av. P = Available phosphorus concentration in soil

[d] $p < 0.01$ 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 factor[a]	
			As	Cd	As	Cd
Angelica gigas	12	Max	4.31	0.39	21.3	18.6
		Min	0.01	0.06	0.005	1.26
		Mean	0.88[ab]	0.24[ab]	2.60[ab]	8.62[ab]
Astragalus membranaceus	11	Max	2.77	0.17	3.27	8.12
		Min	0.14	0.13	0.12	0.75
		Mean	1.48[a]	0.16[b]	0.96[ab]	2.78[b]
Atractylodes macrocephala Koidzumi	14	Max	2.62	0.40	2.78	21.7
		Min	0.02	0.04	0.02	0.42
		Mean	1.38[a]	0.21[b]	0.78[ab]	7.20[ab]
Codonopsis lanceolata	14	Max	0.59	0.33	0.17	8.37
		Min	0.01	0.02	0.009	4.75
		Mean	0.14[bc]	0.22[b]	0.074[b]	5.73[ab]
Platycodon grandiflorum	18	Max	0.21	0.57	0.077	9.49
		Min	0.01	0.21	0.002	4.06
		Mean	0.08[c]	0.34[a]	0.029[b]	6.97[ab]
Rehmannia glutinosa	15	Max	2.42	0.38	13.0	17.5
		Min	0.02	0.03	0.002	1.14
		Mean	1.38[a]	0.17[b]	3.22[a]	11.1[a]
Permissible safety level[b]			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 lanceolate* 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 NH_4OAc 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 NH_4OAc 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 (PO_4^{3-}) in soils; it is chemisorbed by Fe and Al oxides, non-crystalline alumino silicates, and to a smaller extent by layer silicate clays. Being the anion of the weak acid H_3AsO_4, 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

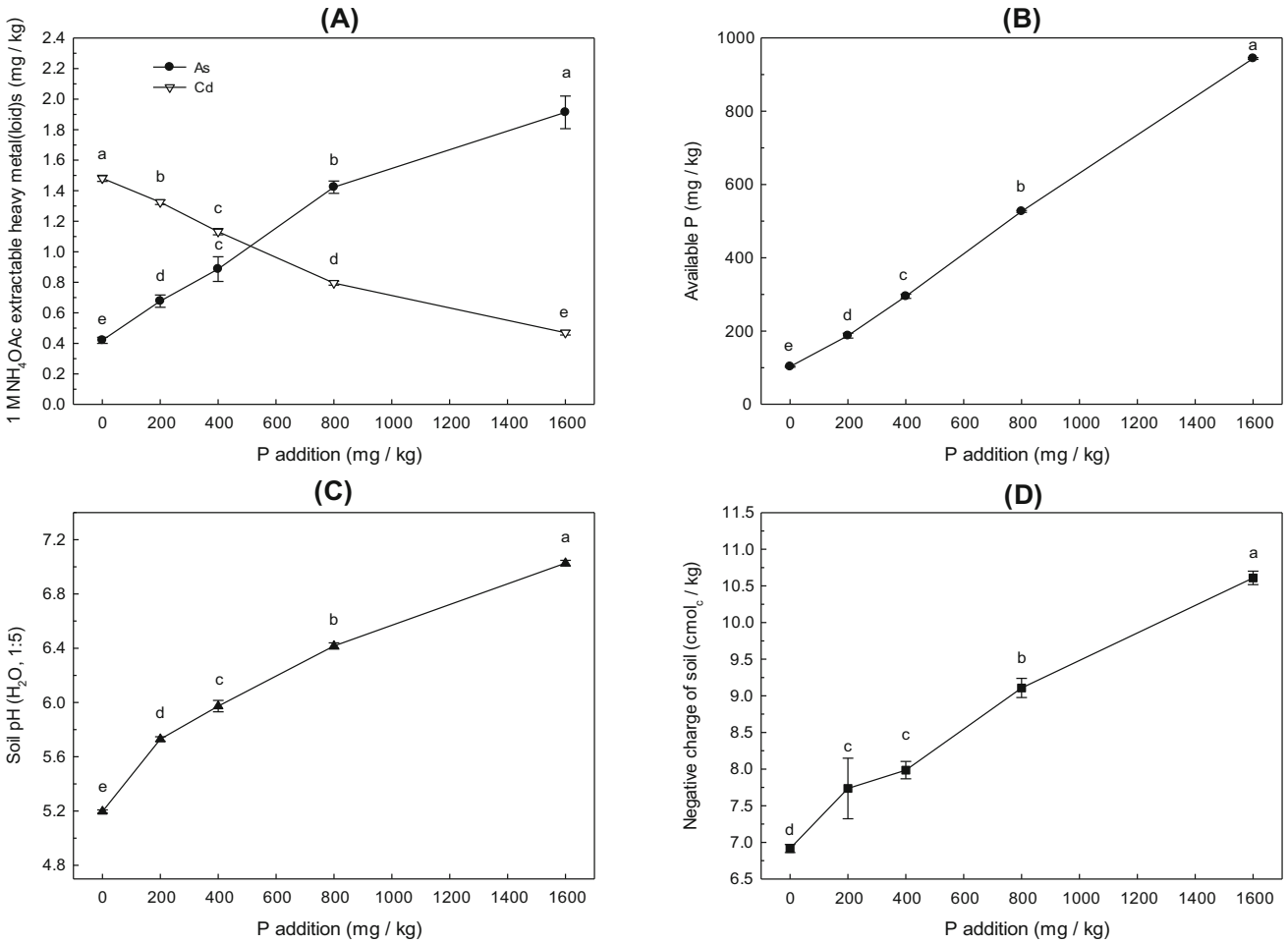

Fig. 6 Changes in 1 M NH_4OAc extractable As and Cd concentrations (**A**), available P concentration (**B**), pH (**C**), negative charge (**D**) of soil added with different rates of K_2HPO_4 after 8 weeks of incubation at 25 °C

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_4OAc extractable As with P addition, 1 M NH_4OAc 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.

Acknowledgment This study was carried out with the support of "Research Program for Agricultural Science & Technology Development (Project No. PJ010827042015)," National Academy of Agricultural Science, Rural Development Administration, Republic of Korea.

References

1. Susanti S, Iwasaki H, Itokazu Y, Nago M, Taira N, Saitoh S, Oku H (2012) Tumor specific cytotoxicity of arctigenin isolated from herbal plant *Arctium lappa* L. Nat Med 66:614–621
2. Stewart MJ, Moar JJ, Steenkamp P, Kokot M (1999) Findings in fatal cases of poisoning attributed to traditional remedies in South Africa. Forensic Sci Int 101:177–183
3. Ernst E (2002) Toxic heavy metals and undeclared drugs in Asian herbal medicines. Trends Pharmacol Sci 23:136–139
4. Dargan PI, Gawarammana IB, Archer JR, House IM, Shaw D, Wood D (2008) Heavy metal poisoning from ayurvedic traditional medicines: an emerging problem. Int J Environ Health 2(3):463–474
5. Dunbabin DW, Tallis GA, Popplewell PY (1992) Lead poisoning from India herbal medicine. Med J Aust 157(11–12):835–836
6. Markowitz SB, Nenez CM, Klitzman S (1994) Lead poisoning due to hai ge fen: the porphyry content of individual erythrocytes. JAMA 271:932–934
7. Olujohungbe A, Fields PA, Sandford AF (1994) Heavy metal intoxication from homeopathic and herbal remedies. Postgrad Med J 70:764–769
8. Kákosy T, Hudák A, Náray M (1996) Lead intoxication epidemic caused by ingestion of contaminated ground paprika. Clin Toxicol 34:507–511
9. Saper RB, Kales SN, Paquin J, Burns MJ, Eisenberg DM, Davis RB, Phillips RS (2004) Heavy metal content of ayurvedic herbal medicine products. JAMA 292:2868–2873
10. Street RA (2012) Heavy metals in medicinal plant products—an African perspective. S Afr J Bot 82:67–74
11. Mazumder DN, Das Gupta J, Santra A, Pal A, Ghose A, Sarkar S (1998) Chronic arsenic toxicity in West Bengal—the worst calamity in the world. J Indian Med Assoc 96:4–7
12. Horiguchi H, Teranishi H, Niiya K, Aoshima K, Katoh T, Sakuragawa N, Kasuya M (1994) Hypoproduction of erythropoietin contributes to anemia in chronic cadmium intoxication: clinical study on itai-itai disease in Japan. Arch Toxicol 68:632–636
13. Nordberg G (1999) Excursions of intake above ADI: case study on cadmium. Regul Toxicol Pharmacol 30:S57–S62
14. McLaughlin MJ, Parkerb DR, Clarkec JM (1999) Metals and micronutrients-food safety issues. Field Crops Res 60:143–163
15. Park BJ, Lee JH, Kim WI (2012) Influence of soil characteristics and arsenic, cadmium, and lead contamination on their accumulation levels in rice and human health risk through intake of rice grown nearby abandoned mines. Appl Biol Chem 54(4):575–582
16. Tripathi RD, Srivastava S, Mishra S, Singh N, Tuli R, Gupta DK, Maathuis FJ (2007) Arsenic hazards: strategies for tolerance and remediation by plants. Trends Biotechnol 25:158–165
17. 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
18. Hong CO, Gutierrez J, Yun SW, Lee YB, Chan Yu, Kim PJ (2009) Heavy metal contamination of arable soil and corn plant in the vicinity of a zinc smelting factory and stabilization by liming. Arch Environ Contam Toxicol 56:190–200
19. Hong CO, Lee DK, Kim PJ (2008) Feasibility of phosphate fertilizer to immobilize cadmium in a field. Chemosphere 70:2009–2015
20. 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. Environ Qual 7:286–290
21. McBride M, Sauve S, Hendershot W (1997) Solubility control of Cu, Zn, Cd and Pb in contaminated soils. Eur J Soil Sci 48:337–346
22. Liu F, De Cristofaro A, Violante A (2001) Effect of pH, phosphate and oxalate on the adsorption/desorption of arsenate on/from goethite. Soil Sci 166:197–208
23. Bolan NS, Adriano DC, Duraisamy A, Mani A, Arulmozhiselvan K (2003) Immobilization and phytoavailability of cadmium in variable charge soils. I. Effect of phosphate addition. Plant Soil 250:83–94
24. Thawornchaisit U, Polprasert C (2009) Evaluation of phosphate fertilizers for the stabilization of cadmium in highly contaminated soils. J Hazard Mater 165:1109–1113
25. 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
26. Jeanjean J, Rouchaud JC, Tran L, Fedoroff M (1995) Sorption of uranium and other heavy mteals on hydroxyapatite. J Radioanal Nucl Chem 201:529–539
27. Mandjiny S, Matis KA, Fedoroff M, Jeanjean J, Rouchaud JC, Toulhoat N, Potocek 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
28. Loganathan P, Hedley MJ, Grace ND, Lee J, Cronin SJ, Bolan NS, Zanders JM (2003) Fertiliser contaminants in New Zealand

grazed pasture with special reference to cadmium and fluorine—a review. Soil Res 41:501–532
29. McGrath D, Tunney H (2010) Accumulation of cadmium, fluorine, magnesium, and zinc in soil after application of phosphate fertilizer for 31 years in a grazing trial. J Plant Nutr Soil Sci 173:548–553
30. Brady NC, Weil RR (2010) Nutrient cycles and soil fertility. In: Elements of the nature and properties of soils, 3rd edn. Pearson, New Jersey, pp 420
31. RDA (Rural Development Administration, Korea) (1988) Methods of soil chemical analysis. National Institute of Agricultural Science and Technology, RDA, Suwon
32. SAS Institute Inc (2008) User's guide: statistics. SAS version 9.4. SAS Institute, Cary
33. Software Analytical (2008) Statistix 9 user's manual. Analytical Software, Tallahassee
34. McBride MB (1994) Trace and toxic elements in soils. In: Environmental chemistry of soils. Oxford University Press, Inc., pp 308–341
35. Xu XY, McGrath SP, Meharg A, Zhao FJ (2008) Growing rice aerobically markedly decreases arsenic accumulation. Environ Sci Technol 42:5574–5579
36. Peryea FJ, Kammereck R (1997) Phosphate-enhanced movement of arsenic out of lead arsenate-contaminated topsoil and through uncontaminated subsoil. Water Air Soil Pollut 93:243–254
37. Peryea FJ (1991) Phosphate-induced release of arsenic from soils contaminated with lead arsenate. Soil Sci Soc Am J 5:1301–1306
38. Levi-Minzi R, Petruzzelli G (1984) The influence of phosphate fertilizers on Cd solubility in soil. Water Air Soil Pollut 23:423–429
39. Cao X, Ma LQ, Shiralipour A (2003) Effects of compost and phosphate amendments on arsenic mobility in soils and arsenic uptake by the hyperaccumulator, *Pteris vittata* L. Environ Pollut 126:157–167
40. Hong CO, Lee HH (2014) Phosphate associated cadmium immobilization mechanism depending on the original concentration of Cd in soil. Korean J Soil Sci Fertil 49:429–433
41. Khan MJ, Jones DL (2009) Effect of composts, lime and diammonium phosphate on the phytoavailability of heavy metals in a copper mine tailing soil. Pedosphere 19:631–641
42. Gutierrez J, Hong CO, Lee BH, Kim PJ (2010) Effect of steelmaking slag as a soil amendment on arsenic uptake by radish (*Raphanus sativa* L.) in an upland soil. Biol Fertil Soils 46:617–623