# Arsenic reactions and brake fern (*Pteris vittata* L.) uptake in tropical soils

Hue Van NGUYEN\*, Amjad AHMAD

Department of Tropical Plant and Soil Sciences, University of Hawaii at Manoa, Honolulu, USA

\*Corresponding author: nvhue@hawaii.edu

### ABSTRACT

Nguyen H.V., Ahmad A. (2017): Arsenic reactions and brake fern (*Pteris vittata* L.) uptake in tropical soils. Plant Soil Environ., 63: 55–61.

In Hawaii, past use of arsenical pesticides has left elevated levels of arsenic (As) in some soils. Sorption isotherms of an Andosol and an Acrisol showed that the former required 1100 mg/kg, and the latter 300 mg/kg of added As to maintain 0.20 mg As/L in solution, the maximum allowable As level in streams/rivers in Hawaii. Greenhouse experiments were conducted on an Andosol (315 mg/kg total As), which was amended with 0, 5 g/kg compost, 5 g Fe/kg as amorphous Fe(OH)<sub>3</sub>, or 250 mg P/kg as Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>, and on a low-As (15 mg/kg) Acrisol, which was spiked with 0, 150 or 300 mg As/kg as Na<sub>2</sub>HAsO<sub>4</sub>·7 H<sub>2</sub>O. Brake fern (*Pteris vittata* L.) was used as the test plant. Arsenic concentration in the fern fronds averaged 355 mg/kg in the Andosol, and 2610 and 1270 mg/kg (from consecutive plantings, 2 and 12 months after As addition, respectively) in the Acrisol spiked with 300 mg/kg of As. Chemical reactions, as suggested by sequential extractions, likely controlled the availability and uptake of soil As. Mehlich-3 extraction could be used to identify As-contaminated soils and potential phytoremediation as it correlated well with bioaccessible As and with As in fern fronds.

Keywords: soil arsenic; toxicity; sorption-desorption; amorphous iron-hydroxides

Arsenic (As) is a serious global environmental toxicant that has poisoned many people unknowingly or deliberately (Emsley 2005, Ravenscroft et al. 2009). Symptoms of As toxicity include skin hyperpigmentation, lesions and hardening (keratosis), and to a lesser extent, cancer and neurological disorders (Brucker 2005). Naturally, total As in soils is about 5–10 mg/kg; however, in Hawaii, sodium arsenite (NaAsO<sub>2</sub>) was used to control weeds in sugarcane fields in the first half of the 20th century (Hance 1948), resulting in soil As levels up to several hundreds of mg/kg (average 280 mg/kg, Cutler et al. 2013). Although As can have -3, 0, +3, and +5 oxidation states, its prevalent forms in soils are the inorganic species: arsenate (As5+) under aerobic conditions and arsenite (As<sup>3+</sup>) in reducing environments (e.g., wetland, flooded fields for rice or taro cultivation). Arsenic availability in soils is controlled by soil properties, mainly Al and Fe oxides, clay, organic matter, redox potential, competing ions (particularly phosphate), and pH, with iron hydroxy-oxides (ferrihydrite, goethite, hematite) being the most As adsorbing minerals (Violante and Pigna 2002, Jiang et al. 2005, Violante et al. 2008, Wenzel 2013, Cutler et al. 2014, Dai et al. 2016). It is the various chemical forms of As, rather than its total concentration, that affects As mobility, bioavailability and toxicity (Goh and Lim 2005, Chakrabarty 2015). Sequential extraction is often used to provide operationally defined phase associations of As species (Hartley et al. 2009). Such fractionations help identify some of the main binding sites and assess the potential for remobilization and bioavailability of As in polluted soils (Martin et al. 2007).

Plants can take up both  $As^{5+}$  and  $As^{3+}$  (inside the plant, most  $As^{5+}$  is then reduced to  $As^{3+}$  before

being further processed, such as translocation from root to shoot or detoxification). In soils and aqueous solutions, As5+ is present mostly as  $H_2AsO_4^-$  and  $HAsO_4^{2-}$ , depending on pH (pK<sub>a</sub>'s of  $H_3$ AsO<sub>4</sub> are 2.3, 7.0, and 11.5). Chemically, arsenate and phosphate (P), whose p $K_a$ 's = 2.1, 7.2, and 12.7, are very similar. Thus, As<sup>5+</sup> can enter cells via P transporters (Hue 2015), and can replace P in many vital biomolecules, rendering them dysfunctional. In contrast, As<sup>3+</sup>, which is found mainly as the neutral  $As(OH)_3$  species (its first  $pK_3 = 9.2$ ), would diffuse through cell membrane-spanning channels created by aquaglyceroporin proteins, which allow the diffusion of water, glycerol, silicate  $[Si(OH)_4]$ , and other neutral species (Hue 2015). This explains how rice plants, which need relatively large quantity of silicate for their structural sturdiness, may contain elevated concentration of As in their grains when grown in As-contaminated soil/water situations (Gupta and Khan 2015); and the use of silica rich amendments can reduce As in rice grain (Seyfferth et al. 2016).

Arsenic concentrations in plants are largely species-, even cultivar-, specific and are usually less than 1.0 mg/kg for most plants growing on non As-contaminated soils (Tlustoš et al. 2006, Kabata-Pendias 2011). However, in As-contaminated sites, even excluder plants may accumulate significant amount (tens to hundreds mg/kg) of total As (Kabata-Pendias 2011). A report from Japan (Kitagishi and Yamane 1981) showed that rice leaves had 7-18 mg As/kg, yielding almost 1.0 mg As/kg in grains. Arsenic hyperaccumulation can be found in a few species of ferns, such as Pteris vittata, P. cretica, P. longifolia, P. umbrosa (Huang et al. 2008, Hue 2015, Das et al. 2017). Among those, P. vittata (Chinese brake fern) is the most recognized and studied; its fronds can contain in excess of 1% (10 000 mg/kg) of As (Ma et al. 2001, Wang et al. 2002). Wang et al. (2007) measured As concentration in ferns collected at different locations in South China (GuangXi province) and found genotypic variations within P. vittata that could be useful in breeding improved cultivars.

Since plants absorb As mostly from soil solution, it is necessary to assess soil As availability for phytoremediation purpose. Many chemical extraction methods were developed to estimate As availability in soils, ranging from sequential extraction (Wenzel et al. 2001) to sorption isotherm (Hue 2013). Gonzaga et al. (2012) used water, am-

monium sulfate, organic acids (a combination of phytic and oxalic acids), ammonium phosphate, and Mehlich 3 extractant (1984) to predict As availability to *P. vittata* grown on As-contaminated soils of Florida. They found that the organic acid solution was the best predictor, whereas Mehlich 3 solution was effective but somewhat overestimated As uptake for the five sandy soils studied.

The objectives of this study were: (1) to examine As reactions in tropical soils, which are high in clays and metal sesquioxides, by using sorption and desorption isotherms and chemical extractions, and (2) to evaluate the use of *P. vittata* in taking up As in contaminated soils of Hawaii via different soil amendments for phytoremediation purpose.

## **MATERIAL AND METHODS**

Soil collection and characterization. Surface samples (0-20 cm depth) of an Acrisol and an Andosol were collected from three sites (one site was contaminated with As, the other two were not) for this study. The Andosol (in the USDA soil taxonomy, it is classified as Ola'a series, ferrihydritic, isohyperthermic Typic Hydrudand) is a product of weathered basalt of volcanic origin. It is rich in organic matter (10.7% organic carbon) and low bulk density (0.62 g/cm<sup>3</sup>). The dominant solid phase materials are iron hydroxy-oxides (ferrihydrite, goethite), allophane, and amorphous gels (Cutler et al. 2013). The soil pH was 5.8 with a total As of 315 mg/kg for the As contaminated sample and 22 mg/kg for the non-contaminated sample. The Acrisol (in the USDA soil taxonomy, it is classified as Leilehua series, ferruginous, isothermic Ustic Kanhaplohumult) was formed from highly weathered igneous rock. It has approximately 30% iron oxides (mainly goethite and hematite), kaolinite and minor amount (< 0.1%) of manganese oxide. The soil pH was initially 4.8, but was limed to 5.7 with CaCO<sub>3</sub>. It has about 2.2% organic carbon, a bulk density of 1.1 g/cm<sup>3</sup> and 15 mg/kg total As. A portion of the soil was spiked with sodium arsenate (Na<sub>2</sub>HAsO<sub>4</sub>·7 H<sub>2</sub>O) to raise total As to 165 and 315 mg/kg and was subjected to many wetting-drying cycles before being used in greenhouse experiments (described later).

Arsenic sorption and desorption isotherms. The two low-As soils were used to construct sorption isotherms. A 2.00 g sample of finely ground

(< 1 mm diameter) soil was equilibrated with 20 mL of 0.01 mol/L  $\operatorname{CaCl}_2$  containing various concentrations of As + 5 as  $\operatorname{Na}_2\operatorname{HAsO}_4$ . The samples were shaken continuously for 6 days following the method proposed for P sorption by Fox and Kamprath (1970). Sorbed As was calculated as the difference between the initially added As and As remaining in solution.

Arsenic desorption was performed on the two high-As (315 mg/kg) soils. A 2.00 g sample was first shaken in 20 mL of 0.01 mol/L  $\operatorname{CaCl}_2$  for 1 h, centrifuged at 5 000 g to obtain the supernatant for As measurement (extraction cycle 1). The solid fraction was sonicated in 20 mL of 0.01 mol/L  $\operatorname{CaCl}_2$  for 2 min and shaken for 1 h, then centrifuged again to obtain supernatant 2 (cycle 2). Eight more cycles were similarly performed, yielding a total of 10 extractions. Both sorption and desorption experiments were run in duplicate.

Chemical analysis of arsenic. Total soil As: A  $1.00~\rm g$  soil was added to a solution of  $10~\rm mL$  concentrated HNO $_3~\rm and~5~\rm mL$  of  $30\%~\rm H_2O_2$ , heated to  $160^{\rm o}\rm C$  for  $2~\rm h$ , diluted to  $50~\rm mL$  with deionized water, and filtered (USEPA method  $3050\rm B$ ). Arsenic in the filtrate was measured with an inductively coupled plasma (ICP) spectrometer with dual detection modes (PerkinElmer model Optima  $7000\rm DV$ , PerkinElmer Life and Analytical Sciences, USA).

Fractional As (sequential extraction): Four different extractants were used sequentially to extract As from the two high-As soils (315 mg/kg): (1) a 2.00 g sample was first shaken with 20 mL of 0.10 mol/L CaCl<sub>2</sub> for 24 h, then centrifuged at 5000 g to obtain the exchangeable fraction; (2) the solid fraction was sonicated in 20 mL of 0.10 mol/L sodium pyrophosphate and shaken for 24 h, and then was centrifuged to obtain the organic matter-associated As fraction; (3) step No. 2 was repeated, but with 20 mL of 0.30 mol/L NH<sub>4</sub>-oxalate, and shaken in the dark to obtain the As associated with amorphous Al and Fe oxides; (4) step No. 2 was repeated, but with 20 mL of 8 mol/L HNO<sub>3</sub> to obtain the 'recalcitrant' As fraction.

Bioaccessible As: A 1.00 g sample was shaken in 100 mL of HCl adjusted to pH 1.5 for 1 h at 37°C. The method was similar to the gastric phase extraction of the Solubility and Bioavailability Research Consortium (Drexler and Brattin 2007), except that no glycine was used and suspension pH was adjusted for each sample with 1 mol/L HCl

immediately before incubation. The suspension was filtered through a 0.45  $\mu m$  membrane and the filtrate was analysed for As with an ICP.

Mehlich 3-extractable As: A 1.00 g soil was added to 10 mL Mehlich 3 solution (0.2 mol/L CH<sub>3</sub>COOH, 0.25 mol/L NH<sub>4</sub>NO<sub>3</sub>, 15 mmol NH<sub>4</sub>F, 13 mmol HNO<sub>3</sub>, and 1 mmol EDTA), shaken for 5 min, filtered for As measurement with an ICP.

All As measurements (total, fractional, bioaccessible, Mehlich 3-extractable) were run in duplicate. Sample blank and reference As standards were checked and adjusted, if necessary, at every 20 samples.

Arsenic uptake by brake fern (Pteris vittata L.). There were two greenhouse experiments. The first experiment used an Andosol containing 315 mg/kg total, 'resident' As, which was added many years ago. The objective was to examine the As uptake of P. vittata under four soil amendments: control, 250 mg P/kg as reagent-grade  $Ca(H_2PO_4)_2$ , 5 g Fe/kg as amorphous Fe(OH)<sub>3</sub>, 5 g/kg composted chicken manure (5 mg/kg total As and 22 g/kg total P on a dry weight basis). The second experiment used an Acrisol with 15 mg/kg total, 'resident' As and being spiked with 0, 150, and 300 mg/kg As as Na<sub>2</sub>HAsO<sub>4</sub>·7 H<sub>2</sub>O to attain a total As level equal to that of the Andosol. Two plantings of *P. vittata* were performed in experiment 2: the first planting was at 2 months after As addition, the second planting was at 12 months after As addition. The objective was to evaluate the aging effect of As salt addition and to compare As uptake between the two soils.

Each experimental pot contained 2 kg soil and received 160 mg N/kg from a commercial 16-16-16 fertilizer (basal fertilization). Local brake ferns were transplanted one plant (approximately 7.5 cm tall) per pot. An automatic system of overhead sprinklers was used for watering (twice daily, 10-min interval). Ambient temperatures were  $28 \pm 5^{\circ}\text{C}$  daytime and  $20 \pm 3^{\circ}\text{C}$  night-time. The ferns were cut about 1 cm above ground 10 weeks after transplanting. Roots and shoots were separated for further processing.

Plant-tissue preparation and analysis. The plant biomass was thoroughly washed with tap water, then twice with deionized water before pat dry. Fresh weights were taken before being oven-dried at 70°C for 3 days. Subsequently, dry weights were recorded. The plant materials were finely chopped and ground to pass 0.4-mm sieve. A

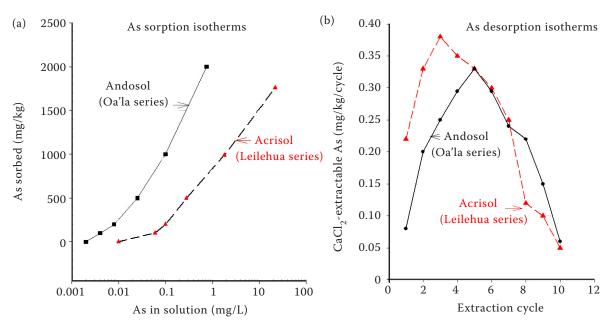


Figure 1. Sorption (a) and desorption (b) of arsenic by two tropical soils of Hawaii

subsample of 0.20 g was ashed in a muffle furnace at 500°C for 4 h. The ash was dissolved in 3 mL of 1 mol/L HNO $_3$  and heated slowly until dry. The residue was redissolved in 10 mL of 0.1 mol/L HCl and filtered before being analysed for As with an ICP. Reagent blanks and internal standards were checked at every 20 samples to ensure accuracy and precision of the analysis.

**Statistical analysis**. The greenhouse experiments had a completely randomized design with three replications per treatment. Analysis of variance (ANOVA) and treatment mean, using the Tukey's significant difference test, were performed with software JMP ® version 11 (SAS, Cary, USA). Graphs were drawn with SigmaPlot ® version 12.5 (Systat, San Jose, USA).

### **RESULTS AND DISCUSSION**

**Sorption and desorption of As in tropical soils of Hawaii**. As Figure 1a illustrates, the Andosol with high content of amorphous Al/Fe hydroxyoxides (i.e., allophane and ferrihydrite) sorbs much more As than the unspiked Acrisol, which contains more crystalline forms of Al/Fe oxides, such as kaolinite, gibbsite, goethite and hematite. For example, in order to maintain 0.20 mg/L of As in solution, a concentration not much different from the maximum level of 0.19 mg/L allowable in streams, rivers by the State of Hawaii (Hawaii Department of Health, 2013, page 23), the Andosol must contain (sorb) approximately 1100 mg As/kg

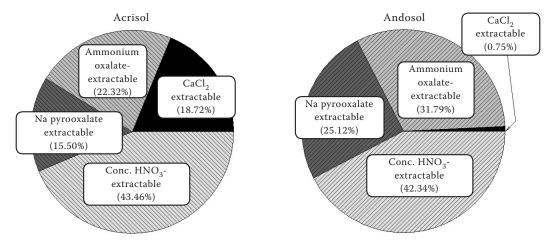


Figure 2. Arsenic (As) fractions as extracted by different solutions from an Andosol and an As-spiked Acrisol, both having 315 mg/kg total As

Table 1. Brake fern (Pteris vittata L.) grown on an Andosol having 315 mg/kg total As subjected to 4 treatments (exp. 1)

Treatment	Dry weight (g/pot)	Frond As (mg/kg)	Root As (mg/kg)
Control	$4.81 \pm 0.86^{\rm bc}$	396 ± 15 <sup>ab</sup>	155 ± 8 <sup>a</sup>
Fe(OH) <sub>3</sub>	$4.35 \pm 1.05^{\circ}$	$214 \pm 20^{b}$	$100 \pm 10^{b}$
Manure	$5.67 \pm 1.32^{ab}$	$385 \pm 24^{ab}$	$85 \pm 6^{c}$
Phosphorus fertilizer	$6.67 \pm 0.20^{a}$	$425\pm25^{\rm a}$	$8 \pm 6^{c}$

Means within a column followed by same letter(s) are not statistically different at 0.05 level, using the Tukey's significant difference test

Table 2. Brake ferns ( $Pteris\ vittata\ L.$ ) grown on an Acrisol having 15 (mg/kg) 'resident' total arsenic (As), which was spiked with 150 or 300 mg/kg As as Na<sub>2</sub>HAsO<sub>4</sub> (experiment 2)

Treatment -	1 <sup>st</sup> planting (2 mont	1st planting (2 months after As addition)		2 <sup>nd</sup> planting (12 months after As addition)	
	dry weight (g/pot)	frond As (mg/kg)	dry weight (g/pot)	frond As (mg/kg)	
Control	$3.75 \pm 1.5^{b}$	$43 \pm 12^{c}$	$3.50 \pm 1.0^{b}$	39 ± 10 <sup>c</sup>	
+ 150 mg/kg As	$5.15 \pm 1.0^{a}$	$1035 \pm 218^{b}$	$5.30 \pm 1.4^{a}$	$439 \pm 87^{\rm b}$	
+ 300 mg/kg As	$3.05 \pm 1.3^{b}$	$2610 \pm 461^{a}$	$3.50 \pm 1.2^{b}$	$1270 \pm 225^{a}$	

Means within a column followed by the same letter(s) are not statistically different at 0.05 level, using the Tukey's significant difference test

as opposed to 300 mg/kg for the Acrisol. Desorption isotherms shown in Figure 1b further support the differential retention of As by the two soils. It takes five extraction cycles to desorb the most quantity of As per cycle for the Andosol, whereas only three cycles were needed to reach the maximum extraction in the As-spiked Acrisol. However, it should be noted that the total quantities of As as extracted by 0.01 mol/L CaCl<sub>2</sub> after 10 cycles were only 0.67% for the Andosol and 0.77% for the Acrisol, suggesting that both soils can sorb As strongly, and provide little bioavailable As.

Such strong As retention could be explained by the reactions between arsenate ions in solution and the solid-phase iron hydroxy-oxides (Kumar et al. 2016). According to Wenzel (2013) and Kumar et al. (2016), Fe-As reactions would form a binuclear bidentate complex if As concentration is relatively high, and a mononuclear bidentate complex if As concentration is low.

In fact, in the Andosol, 31.79% of the total 315 mg/kg As was associated with amorphous Fe-Al oxides (as extracted by ammonium oxalate), only 0.75% was exchangeable (as extracted by CaCl<sub>2</sub>). In contrast, 18.72% of the total As (315 mg/kg) in the spiked Acrisol was exchangeable, and 22.32% was associated with amorphous Fe oxides (Figure 2).

Phytoremediation of soil As using brake fern (*Pteris vittata* L.). Brake ferns grown on the Andosol, which has 315 mg/kg total As as

a result of past (several decades ago) use of arsenical herbicide (NaAsO $_2$ ), had between 214 and 425 mg/kg As on average in the fern frond, depending on soil treatments (Table 1). The P fertilized and manured treatments showed better growth and higher As concentration in fronds than the control and the Fe(OH) $_3$  treatments (Table 1). The results could be explained by the fact that phosphate in P fertilizer and P + organic anions in manure could displace sorbed As into soil solution and make As more available for uptake by the fern. On the other hand, the addition of amorphous Fe(OH) $_3$  further strengthened As sorption, thereby lowering the uptake. Poorer growth in the Fe(OH) $_3$  treatment might have also been caused by a reduced

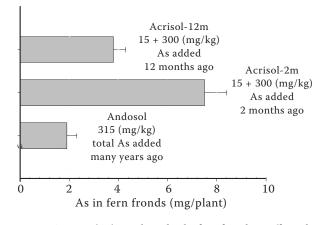
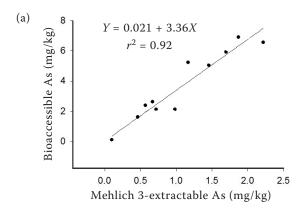


Figure 3. Arsenic (As) uptake in brake fern fronds as affected by different soils and times of equilibration (aging effect)



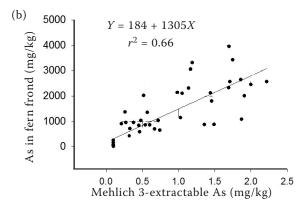


Figure 4. Relationship (a) between Mehlich 3-extractable arsenic (As) and bioaccessible As in Hawaiian soils, and (b) between Mehlich 3-extractable As and As in brake fern fronds

availability of P and other plant nutrients due to their sorption onto  $Fe(OH)_3$ . These As concentrations were at least an order of magnitude lower than those reported by Ma and co-workers for sandy soils in Florida (Ma et al. 2001, Tu and Ma 2003). It appears that As phytoavailability is rather low in this Andosol, probably because of strong reactions between As ions and amorphous Fe and Al minerals in the soil.

Contrary to the Andosol, the Acrisol originally contained only 15 mg/kg total As. By spiking with 150 and 300 mg/kg As and growing ferns 2 and 12 months after As addition, As uptake was drastically increased relative to that in the Andosol (Table 2). Frond As concentrations were only 43 mg/kg (2 months) and 39 mg/kg (12 months) in the control as compared to 2610 mg/kg (2 months) and 1270 mg/kg (12 months) in the treatment spiked with 300 mg/kg As. Using average dry weights of all four treatments in experiment 1 where the soil was high in As, and average dry weights of the two high-As treatments in experiment 2, it was calculated that As uptake by brake ferns ranged from 1.9 to 7.0 mg/plant during the 2½ month growth period. The uptake was highest in the Acrisol with newly added (2 months) As (Figure 3).

The soils were also extracted with Mehlich 3 solution, and selected samples were extracted by both Mehlich 3 and HCl, pH 1.5,  $37^{\circ}$ C (bioaccessible As) for comparison. There was a strong correlation ( $r^2 = 0.92$ ) between bioaccessible As and Mehlich 3 extractable As (Figure 4a). Although containing some strong chelating agents (i.e., EDTA and fluoride ions), Mehlich 3-extraction method possesses shorter shaking time (5 min vs. 1 h) and narrower soil-to-solution ratio (1:10 vs. 1:100) than the extraction method for bioaccessible As,

that partially explains why Mehlich 3 extractable As was about 3.3 times less than bioaccessible As at least for high-clay soils of Hawaii (Figure 4a). On the other hand, Mehlich-3 As correlated fairly positively well ( $r^2 = 0.66$ ) with As concentration in fern fronds (Figure 4b). The result was in agreement with those of Gonzaga et al. (2012), who worked with five sandy soils of Florida.

In conclusion, past use of arsenical pesticides has resulted in high As in some areas of Hawaii. Andosols with high proportions of amorphous Al and Fe hydroxy-oxides can retain As strongly and make it less bioavailable. Newly added As to an Acrisol having more crystalline Al/Fe minerals was more available for uptake by brake ferns. The uptake, however, declined with time. Phosphate fertilizer and manure increased As availability to *P. vittata* whereas amorphous iron oxide reduced it. Mehlich 3 extractable As was much lower (3.3 fold) than bioaccessible As, but could be used as a rough predictor of As uptake by the brake fern grown in high As, high sesquioxide soils of Hawaii.

## **REFERENCES**

Buchet J.P. (2005): Arsenic speciation in human tissues. In: Cornelis R., Crews H., Caruso J., Heumann K.G. (eds.): Handbook of Elemental Speciation II: Species in the Environment, Food, Medicine and Occupational Health. New York, John Wiley and Sons, 86–93.
Chakrabarty N. (2015): Introduction to arsenic toxicity. In: Chakrabarty N. (ed.): Arsenic Toxicity: Prevention and Treatment. Boca Raton, CRC Press, 3–16.

Cutler W.G., Brewer R.C., El-Kadi A., Hue N.V., Niemeyer P.G., Peard J., Ray C. (2013): Bioaccessible arsenic in soils of former sugar cane plantations, island of Hawaii. Science of the Total Environment, 442: 177–188.

- Cutler W.G., El-Kadi A., Hue N.V., Peard J., Scheckel K., Ray C. (2014): Iron amendments to reduce bioaccessible arsenic. Journal of Hazardous Materials, 279: 554–561.
- Dai M., Xia L., Song S.X., Peng C.S., Lopez-Valdivieso A. (2016): Adsorption of As(V) inside the pores of porous hematite in water. Journal of Hazardous Materials, 307: 312–317.
- Das S., Chou M.L., Jean J.S., Yang H.J., Kim P.J. (2017): Arsenic-enrichment enhanced root exudates and altered rhizosphere microbial communities and activities in hyperaccumulator *Pteris vittata*. Journal of Hazardous Materials, 325: 279–287.
- Drexler J.W., Brattin W.J. (2007): An *in vitro* procedure for estimation of lead relative bioavailability: With validation. Human and Ecological Risk Assessment: An International Journal, 13: 383–401.
- Emsley J. (2005): The Elements of Murder. Oxford, Oxford University Press, 93–193.
- Fox R.L., Kamprath E.J. (1970): Phosphate sorption isotherms for evaluating the phosphate requirements of soils. Soil Science of Society of America Journal, 34: 902–907.
- Goh K.H., Lim T.T. (2005): Arsenic fractionation in a fine soil fraction and influence of various anions on its mobility in the subsurface environment. Applied Geochemistry, 20: 229–239.
- Gonzaga M.I., Ma L.Q., Pacheco E.P., dos Santos W.M. (2012): Predicting arsenic bioavailability to hyperaccumulator *Pteris vittata* in arsenic-contaminated soils. International Journal of Phytoremediation, 14: 939–949.
- Gupta M., Khan E. (2015): Mechanism of arsenic toxicity and tolerance in plants: Role of silicon and signalling molecules. In: Tripathi B.N., Muller M. (eds.): Stress Responses in Plants: Mechanisms of Toxicity and Tolerance. Cham, Springer, 143–157.
- Hance F.E. (1948): Weed control on Hawaiian sugar-cane lands Contact herbicides. The Hawaiian Planters' Record, 52: 93–112.
- Hartley W., Dickinson N.M., Clemente R., French C., Piearce T.G., Sparke S., Lepp N.W. (2009): Arsenic stability and mobilization in soil at an amenity grassland overlying chemical waste (St. Helens, UK). Environmental Pollution, 157: 847–856.
- Hawaii Department of Health (2013): Water quality standards. Chapter 54 of title 11, p. 23. http://health.hawaii.gov/cwb/files/2013/05/PN\_20140826\_1154Proposed.pdf (accessed June 9, 2016)
- Huang Z.C., Chen T.B., Lei M., Liu Y.R., Hu T.D. (2008): Difference of toxicity and accumulation of methylated and inorganic arsenic in arsenic-hyperaccumulating and -hypertolerant plants. Environmental Science Technology, 42: 5106–5111.
- Hue N.V. (2013): Arsenic chemistry and remediation in Hawaiian soils. International Journal of Phytoremediation, 15: 105–116.
- Hue N.V. (2015): Bioremediation of arsenic toxicity. In: Chakrabarty N. (ed.): Arsenic Toxicity: Prevention and Treatment. Boca Raton, CRC Press, 155–165.
- Jiang W., Zhang S., Shan X.Q., Feng M., Zhu Y.G., McLaren R.G. (2005): Adsorption of arsenate on soils. Part 1: Laboratory batch experiments using 16 Chinese soils with different physicochemical properties. Environmental Pollution, 138: 278–284.
- Kabata-Pendias A. (2011): Trace Elements in Soils and Plants. Boca Raton, CRC Press.
- Kitagishi K., Yamane I. (1981): Heavy Metal Pollution in Soils of Japan. Tokyo, Japan Science Society Press.

- Kumar S.P., Flores R.Q., Sjöstedt C., Önnby L. (2016): Arsenic adsorption by iron-aluminum hydroxide coated onto macroporous supports: Insights from X-ray absorption spectroscopy and comparison with granular ferric hydroxides. Journal of Hazardous Materials, 302: 166–174.
- Ma L.Q., Komar K.M., Tu C., Zhang W., Cai Y., Kennelley E.D. (2001): A fern that hyperaccumulates arsenic: A hardly, versatile, fast-growing plant helps to remove arsenic from contaminated soils. Nature, 409: 579.
- Martin M., Violante A., Barberis E. (2007): Fate of arsenite and arsenate in flooded and not flooded soils of southwest Bangladesh irrigated with arsenic contaminated water. Journal of Environmental Science and Health. Part A, Toxic/Hazardous Substances and Environmental Engineering, 42: 1775–1783.
- Mehlich A. (1984): Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. Communications of Soil Science and Plant Analysis, 15: 1409–1416.
- Ravenscrof P., Brammer H., Richards K. (2009): Arsenic in Asia. In: Ravenscrof P., Brammer H., Richards K. (eds.): Arsenic Pollution: A Global Synthesis. Oxford, Wiley-Blackwell.
- Seyfferth A.L., Morris A.H., Gill R., Kearns K.A., Mann J.N., Paukett M., Leskanic C. (2016): Soil incorporation of silica-rich rice husk decreases inorganic arsenic in rice grain. Journal of Agricultural Food Chemistry, 64: 3760–3766.
- Tlustoš P., Száková J., Hrubý J., Hartman I., Najmanová I., Nedělník J., Pavlíková D., Batysta M. (2006): Removal of As, Cd, Pb, and Zn from contaminated soil by high biomass producing plants. Plant, Soil and Environment, 52: 413–423.
- Tu C., Ma L.Q. (2003): Effects of arsenate and phosphate on their accumulation by an arsenic-hyperaccumulator *Pteris vittata* L. Plant and Soil, 249: 373–382.
- Violante A., Gaudio S.D., Pigma M., Pucci M., Amalfitano C. (2008): Sorption and desorption of arsenic by soil minerals and soils in the presence of nutrients and organics. In: Huang X., Huang P.M., Violante A. (eds.): Soil Mineral-Microbe-Organic Interactions. Berlin, Springer-Verlag, 39–69.
- Violante A., Pigna M. (2002): Competitive sorption of arsenate and phosphate on different clay minerals and soils. Soil Science Society of America Journal, 66: 1788–1796.
- Wang H.B., Wong M.H., Lan C.Y., Baker A.J., Qin Y.R., Shu W.S., Chen G.Z., Ye Z.H. (2007): Uptake and accumulation of arsenic by 11 *Pteris* taxa from southern China. Environmental Pollution, 145: 225–233.
- Wang J.R., Zhao F.J., Meharg A.A., Rabb A., Feldman J., McGrath S.P. (2002): Mechanisms of arsenic hyperaccumulation in *Pteris* vittata. Uptake kinetics, interactions with phosphate, and arsenic speciation. Plant Physiology, 130: 1552–1561.
- Wenzel W.W. (2013): Arsenic. In: Alloway B.J. (ed.): Heavy Metals in Soils: Trace Metals and Metalloids in Soils and their Bioavailability. Environmental Pollution, 22. Dordrecht, Springer Science, 241–282.
- Wenzel W.W., Kirchbaumer N., Prohaska T., Stingeder G., Lombi E., Adriano D.C. (2001): Arsenic fractionation in soils using an improved sequential extraction procedure. Analytica Chimica Acta, 436: 309–323.

Received on June 15, 2016 Accepted on January 17, 2017 Published online on February 24, 2017