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Arsenic Reactions and Plant Uptake in Hawaiian Soils

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Abstract: Arsenic (As) is toxic to most living organisms. In Hawaii, although agricultural uses of arsenical pesticides had been stopped many decades ago, elevated levels of arsenic remain in some soils. Given the volcanic ash origin and fast weathering conditions of Hawaii, Hawaiian soils often contain high amounts of amorphous aluminosilicates and iron oxides, which can sorb and retain As strongly. More specifically, As sorption isotherms that were performed on eight soils of different soil orders showed that Andisols, particularly Hydrudands, sorb most As, followed by Oxisols and Ultisols, whereas Mollisols and Vertisols , consisting mostly of 2:1 layer silicates, sorb least. In an attempt to remove As by plants (phytoremediation), greenhouse experiments were established on an As-contaminated Andisol, which had 315 mg kg^{-1} total As and was amended with 0, 5 g kg^{-1} compost or 250 mg kg^{-1} P as treble superphosphate, and on a low-As Ultisol, which was spiked with 0, 150 or 300 mg kg^{-1} As as Na_2HAsO_4. Chinese brake fern (*Pteris vittata* L.), an As hyperaccumulator, was used as the test plant. Arsenic concentrations in the fern fronds varied on average from 380 mg kg^{-1} in the Andisol to 2600 mg kg^{-1} in the Ultisol, suggesting different chemical reactions and availability of soil As with respect to plant uptake. In fact, bioaccessible As (as extracted with HCl, pH 1.5) and Mehlich-3 extractable As were increased with P amendments and were higher in the Ultisol than in the Andisol having similar total As.

Introduction: Arsenic (As) is a serious global environmental toxicant (Ravencroft et al., 2009). Symptoms of As toxicity include skin hyperpigmentation, lesions and hardening (keratosis), and to a lesser extent, cancer and neurological disorders (Bruchet, 2005).

In Hawaii, sodium arsenite ($NaAsO_2$) was used to control weeds in sugarcane fields from the early 1910s to the late 1940s (Larsen, 1914; Hance,1948). As a result, elevated As levels (20 – 200 mg kg^{-1}) have been identified at a number of locations throughout the State (HDOH, 2010; Hue, 2012; Cutler et al., 2013).

In soils, As is found in -3, 0, +3, and +5 oxidation states. Its prevalent forms are the inorganic species: arsenate (As[+5]) in aerobic environments and arsenite (As [+3] under reducing conditions. Soil As is distributed among different soil components, specifically metal oxides (Al, Fe, Mn oxides) and short-range ordered aluminosilicates (allophane, ferrihydrite, imogolite) (Violante et al., 2008). It is the form of chemical associations of As with various soil solid phases, rather that its total concentration, that affects its mobility, bioavailability and toxicity (Goh and Lim, 2005).

Although many plants do not absorb much As (approximately 0.1 – 5 mg kg^{-1} in leaves), a few do (Schat et al., 2000). The Chinese brake fern (*Pteris vittata* L.) can accumulate between 1440 and 7500 mg kg^{-1} As in its fronds from some As-contaminated sandy soils of Florida (Ma et al., 2001; Tu and Ma, 2003).

Objectives: (1) To gain a good understanding of As reactions in Hawaiian soils, which are often high in clays and metal oxides, and (2) To evaluate the use of brake fern in taking up soil As under different amendments/conditions for phytoremediation purpose.

Materials and Methods

Soils: Using descriptions of soil map units from the National Resources Conservation Services (NRCS, 2010) and geographic coordinates from a pocket GPS unit, several soil series (surface 1-10 cm samples) were collected for As sorption isotherms. Additionally, an Andisol containing 315 mg kg^{-1} total As and an Ultisol containing 15 mg kg^{-1} As (later spiked with Na_2HAsO_4 to match As level of the Andisol) were collected in bulk for remediation studies.

Chemical Analysis of Arsenic:

Total soil As: 1.00 g soil + 10 mL concentrated HNO_3 and 5 mL of 30% H_2O_2, heated to 160 °C for 2 h., diluted to 50 mL (USEPA method 3050B).

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 (gastric phase extraction of the Solubility and bioavailability Research Consortium).

Mehlich 3-extractable As: 1.00 g soil + 10 mL Mehlich 3 solution, shaken for 5 min., filtered.

Arsenic in filtrates was measured with an Inductively Coupled Plasma (ICP) spectrometer (Perkin-Elmer Optima 7000DV) with dual detection modes.

Arsenic sorption isotherms: 2 .00 g soil + 20 mL of 10 m*M* $CaCl_2$ containing various concentrations of As (+5) as Na_2HAsO_4 , shaken continuously for 6 d. Sorbed As was calculated as the difference between the initially added As and As remaining in solution.

Effects of phosphate on bioaccessible soil As: An Andisol high in As (total As = 450 mg kg^{-1}) was amended with different rates of $Ca(H_2PO_4)_2$ and subjected to two wetting (4 days)-drying (3 days) cycles before subsamples were taken for bioaccessible As extraction and analysis with ICP.

Arsenic uptake by brake fern (*Pteris vittata* L.)

First greenhouse experiment used an Andisol containing 315 mg kg^{-1} total, 'resident' As subjected to 4 treatments: control, 250 mg kg^{-1} P, 5 g kg^{-1} Fe as amorphous $Fe(OH)_3$, 5 g kg^{-1} composted chicken manure (22 g kg^{-1} total P by dry weight). Second greenhouse experiment used an Ultisol with 15 mg kg^{-1} total, 'resident' As and being spiked with 0, 150, and 300 mg kg^{-1} As as Na_2HAsO_4 to attain a total As level equal to that of the Andisol. Local Chinese brake ferns were transplanted one plant (@ 7.5 cm tall) per pot of 2.0 kg soil (1st experiment) or 1.0 kg/pot (2nd experiment).

Results and Discussion

Arsenic sorption of Hawaiian soils

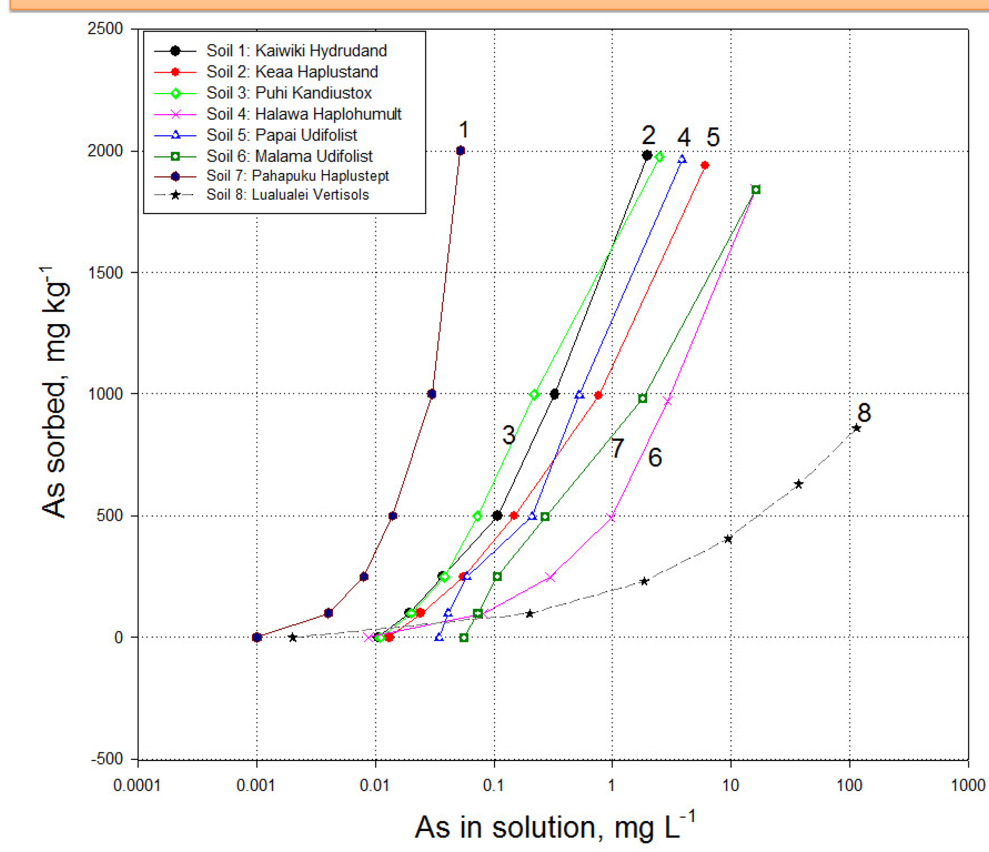
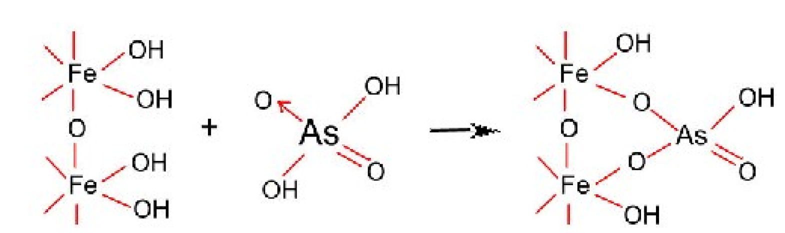


Figure 1. Arsenic sorption isotherms of 8 soils of Hawaii.

Sorption isotherms of 8 soil series are shown in Figure 1. Andisols having considerable quantities of amorphous Fe and Al oxides (e.g., ferihydrite, imogolite, allophane) sorb much more As than Inceptisols or Vertisols, which contain mainly 1:1 and 2:1 layer silicates, respectively. Oxisols and Ultisols, which often have crystalline Al and Fe oxides, such as gibbsite, goethite or hematite, have moderate As sorption capacity, that is weaker than Andisols (particularly the Hydrudand group) but stronger than Vertisols. More interesting is the As sorption of Histosols, which is rather strong, perhaps due to the many sulfhydryl (SH) groups in the large organic component of these soils.

Given the high content of amorphous Fe and Al oxy-hydroxides in Hydrudands (Cutler et al., 2013), it is likely that most As was strongly adsorbed on these oxides, perhaps mainly as binuclear bidentate surface complexes as illustrated below.



Effects of P fertilization on soil As bioaccessibility and potential plant availability

Adding P fertilizers to an high-As Andisol resulted in the release of significant amounts of As (Fig. 2). For example, bioaccessible As increased from 18 to 31 mg kg^{-1} when 450 mg kg^{-1} P as $Ca(H_2PO_4)_2$ was added. Thus, the potential adverse effect of As would be increased considerably if a soil high in As was amended with large quantities of P containing materials (e.g., chemical fertilizer, manure or compost) to promote plant growth as in an urban garden.

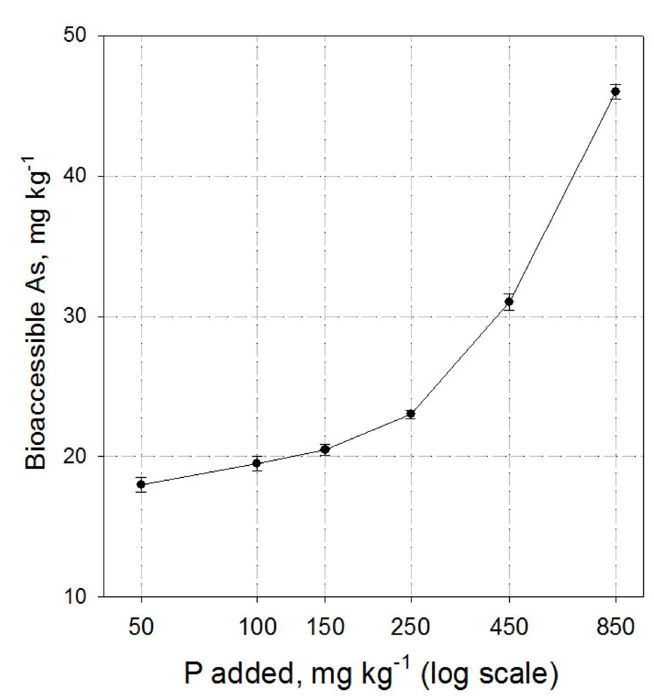


Figure 2. Effect of P fertilizer on HCl-extractable As (bioaccessible As) in an high-As Andisol of Hawaii.

Although bioaccessible As is mainly used to indicate the potential harmful effects of As on humans and animals via ingestion, it is positively and strongly correlated with the Mehlich 3-extractable As, which is an indicator of As availability to plants (Figure 3).

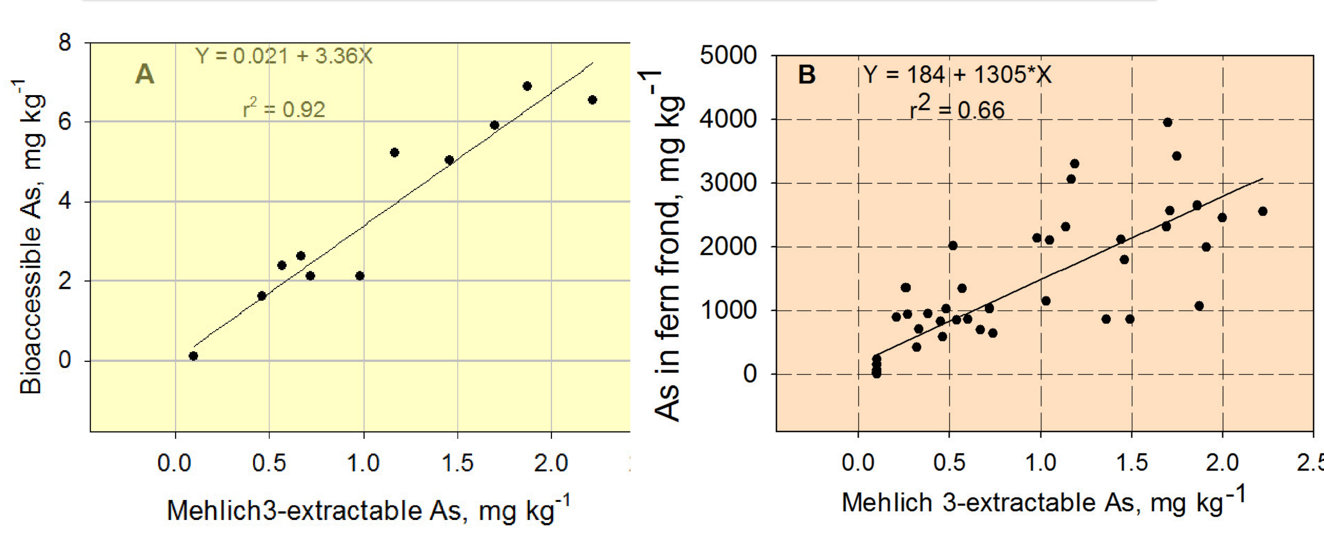


Figure 3. Relationship between Mehlich 3-extractable As and bioaccessible As in Hawaiian soils (A), and between Mehlich 3-extractable As and As in fern fronds (B).

Phytoremediation of soil As using brake fern (*Pteris vittata* L.)

Figure 4. Brake ferns grown on an Andisol with 315 mg kg^{-1} total As subjected to 4 treatments: control, 5 g kg^{-1} Fe as amorphous $Fe(OH)_3$, 250 mg kg^{-1} P, 5 g kg^{-1} composted chicken manure (exp. 1)

Table 1. Brake fern grown on an Andisol having 315 mg kg^{-1} total As subjected to 4 treatments (experiment 1).

Treatment	Dry weight g/pot	Frond As mg kg^{-1}	Root As mg kg^{-1}
Control	7.3 ± 1.3	376 ± 14	155 ± 8
$Fe(OH)_3$	6.6 ± 1.6	233 ± 23	103 ± 10
Manure	8.6 ± 2.0	388 ± 25	81 ± 6
P fertilizer	10.0 ± 0.2	420 ± 25	83 ± 7

Brake ferns grown on the Andisol, which has 315 mg kg^{-1} total As as a result of past (several decades ago) use of arsenical herbicide ($NaAsO_2$), had between 233 and 420 mg kg^{-1} As on average in the fern frond (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 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). The above-ground biomass produced was between 28 and 44 g/pot (fresh weight) after 3 months of growth with a maximum As uptake of 4.6 mg per pot (Figure 4). It appears that As phytoavailability is rather low in this Andisol, probably because of strong reactions between As ions and amorphous Fe and Al minerals in the soil.

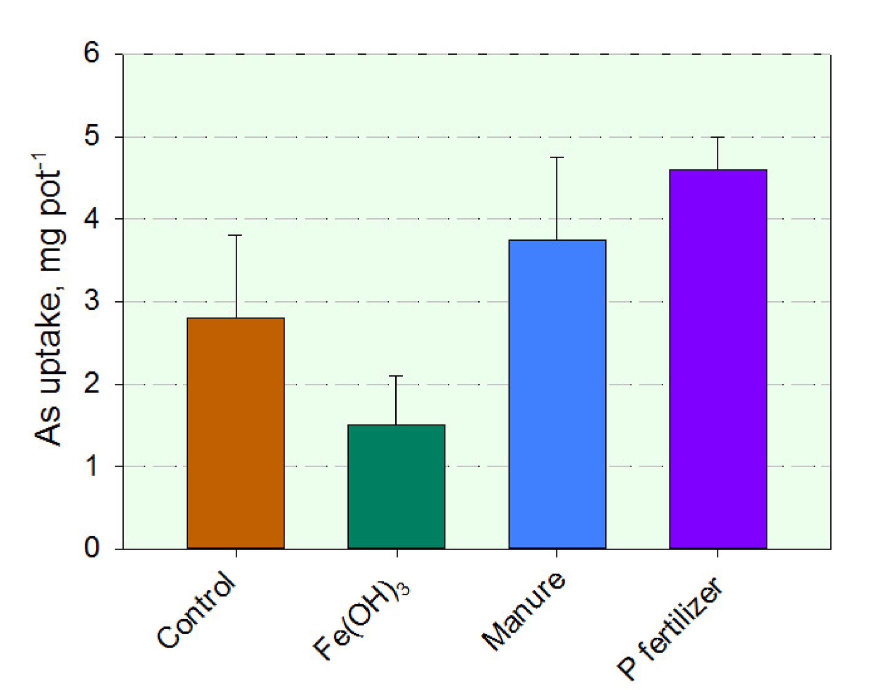


Figure 4. Arsenic uptake by brake fern (above ground biomass) as affected by different soil amendments.

Table 2. Brake ferns grown on an Ultisol having 15 mg kg^{-1} 'resident' total As with 150 or 300 mg kg^{-1} added As (exp. 2).

Treatment	1st planting (2 m. after As addition) Dry weight g/pot	1st planting (2 m. after As addition) Frond As mg kg^{-1}	2nd planting (12 m. after As addition) Frond As mg kg^{-1}
Control	3.75 ± 1.5	43 ± 12	39 ± 10
+ 150 mg kg^{-1} As	5.15 ± 1.0	1035 ± 218	439 ± 87
+ 300 mg kg^{-1} As	3.05 ± 1.3	2610 ± 461	1270 ± 225

Contrary to the Andisol, the Ultisol originally contained only 15 mg kg^{-1} total As. By adding 150 and 300 mg kg^{-1} As and growing ferns 2 and 12 months after As addition, As uptake was drastically increased relative to that in the Andisol (Table 2). Frond As concentrations were only 43 (2 m.) and 39 mg kg^{-1} (12 m.) in the control as compared to 2610 (2 m.) and 1270 mg kg^{-1} (12 m.) in the treatment with 300 mg kg^{-1} added As. The results indicate that (1) soil As was more available in the Ultisol than in the Andisol (at the same level of total As), and (2) longer equilibration time (12 m. vs. 2 m.) reduces As availability, showing a strong aging effect (Figure 5).

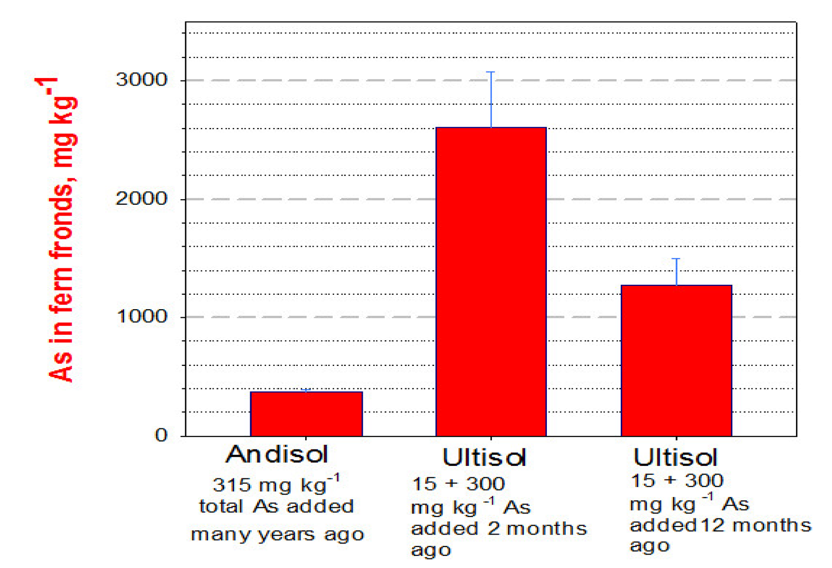


Figure 5. Arsenic concentrations in brake fern fronds as affected by different soils and times of equilibration.

Conclusions. Past use of arsenical pesticides has resulted in high As in some areas of Hawaii. Andisols with high proportions of amorphous aluminosilicates and oxides can retain As strongly and make it less bioavailable. Newly added As to an Ultisol having more crystalline minerals was more available for uptake by brake ferns. The uptake, however, declined with time. Phosphate fertilizer and manure increased As solubility whereas amorphous iron oxide reduced it.

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