Arsenic levels, chemistry and bioavailability in Hawaii soils

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Abstract

Past use of arsenical pesticides has resulted in elevated levels of arsenic (As) in some Hawaii soils. Total As concentrations of 50 -100 mg/kg are not uncommon, and can exceed 900 mg/kg in some former sugarcane lands. Given the high content of amorphous aluminosilicates and iron oxides in many Hawaii Andisols, a high proportion (25 – 30%) of soil As seemed to associate with either these mineral phases or with organic matter. Fractions that are water soluble or exchangeable, thus potentially bioavailable, contributed less than 1% of the total As. In contrast, soils having more crystalline minerals (e.g.Oxisols) often contain less As and also sorb less. Phosphate fertilization increases As bioaccessibility, whereas $Fe(OH)_3$ addition decreases it. Brake fern (*Pteris vittata* L.) could be used to remove some soil As. Concentration of As in fern fronds varied from approximately 40 mg/kg when grown on a low-As Oxisol to 800 mg/kg when grown on a high-As Andisol. The bioaccumulation ratio (plant As/soil As) apparently was rather constant at ~2:1 for this fern.

Key Words

Bioaccessible As, sorption, sequential extraction, phytoremediation.

Introduction

Arsenic (As) is a serious global environmental toxicant (Ravenscroft *et al.* 2009). Chronic exposure to As is known to cause adverse health effects in human, notably skin hyperpigmentation, lesions and hardening (keratosis), and to a lesser extent, cancer and neurological disorders (Ravenscroft *et al.* 2009). In Hawaii, the chemical control of weeds in the sugar industry began in 1913 when experiments with sodium arsenite ($NaAsO_2$) were undertaken on the island of Hawaii. From its first use until about 1945, $NaAsO_2$ dissolved in water was the primary herbicide used on sugarcane fields throughout the State. Although background levels of As in Hawaii soils are typically less than 20 mg/kg, significant elevated As levels have been identifies at a number of locations. In fact, levels of 50 – 100 mg/kg are not uncommon throughout Hawaii. On former sugarcane lands, a broad region has been identified with total soil As as high as 900 mg/kg (Ortiz-Escobar *et al.* 2006). In soils, As is found in -3, 0, +3, and +5 oxidation states. Its prevalent forms are the inorganic species: arsenate (As[+5]) and arsenite (As [+3]). Arsenic may occur in methylated forms but these organic species are much less bio-toxic and rare in soils and surface waters (Smith *et al.* 1998). 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 than its total concentration, that affects its mobility, bioavailability and toxicity (Goh and Lim 2005). Sequential extraction is often used to provide operationally defined phase associations of As species. 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). Many plants do not absorb much As (approximately 1 – 10 mg/kg in leaves), but a few do (Schat *et al.* 2000). The Chinese brake fern (*Pteris vittata* L.) can accumulate between 1,440 and 7,500 mg As/kg in its fronds from some As-contaminated sandy soils of Florida (Ma *et al.* 2001). Arsenic may be taken up as arsenate by the phosphate transport system and subsequently interfering with P-related metabolic processes (Meharg *et al.* 1994; Miteva *et al.* 2005; Ravenscroft *et al.* 2009). Many former sugarcane lands, and some with high As, are being used for commercial agriculture, for residential housing and family gardening, for school and play ground building. Thus, good understanding of As reactions in Hawaii soils is urgently needed so As contaminated soils can be properly managed and remediated, if necessary. That was the objective of this study.

Methods

Survey of As levels in selected Hawaii soils

Using descriptions of soil map units published by the National Resources Conservation Services of America and geographic coordinations, we sampled about two dozen soil samples (series) at 1-10 cm from the surface throughout the Hawaiian Islands. Detailed sampling was performed on an Andisol and an Oxisol.

Chemical analysis of arsenic

Total As: a 1.00 g soil sample was shaken in 50 mL of (30% concentrated HNO_3 and 70% concentrated $HClO_4$) for 24 hours. Arsenic in the filtrate was measured with an inductively coupled plasma spectrometer (ICP). Bioaccessible As: a 1.00 g sample was shaken in 100 mL of HCl adjusted to pH 1.5 for 1 hour at 37 ^{o}C. Fractional As: four different extractants were used sequentially to extract soil As. (1) a 2.00 g sample was first shaken with 20 mL, 0.1 *M* $CaCl_2$ for 24 hours, then centrifuged, to obtain exchangeable fraction; (2) The solid was sonicated in 20 mL, 0.10 *M* sodium pyrophosphate then shaken for 24 hours, and centrifuged (organic matter-associated As); (3) step (2) was repeated, but with 20 mL, 0.30 *M* NH_4-oxalate, and shaken in the dark (amorphous Al and Fe oxides-associated As); (4) step (2) was repeated, but with 20 mL of 8 *M* HNO_3 (recalcitrant As).

Arsenic sorption/desorption and treatments with phosphate or $Fe(OH)_3$

Sorption isotherms of As were constructed by equilibrating 2.00 g soil in 20 mL of 10 m*M* $CaCl_2$ containing various concentrations of As (+5) as Na_2HAsO_4. The samples were shaken continuously for 7 days. Sorbed As was calculated as the difference between the initially added As and As remained in solution. Desorption was carried out by continuously extracting 2.00 g soil with 20 mL of 10 m*M* $CaCl_2$ for 10 times, equilibration time between each extraction was 1 hour. Effects of phosphate or $Fe(OH)_3$ on bioaccessible As were studied by mixing a high-As soil with different rates of $Ca(H_2PO_4)_2$ or amorphous $Fe(OH)_3$, and subjected the treated samples to two wetting (4 days)-drying (3 days) cycles before subsamples were taken for As analysis with ICP.

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

A greenhouse experiment with 4 treatments: [control, 250 mg P/kg, 0.5% Fe as $Fe(OH)_3$, 0.5% compost] was established on a high-As Andisol (300 mg/kg total As) and a low-As Oxisol (18 mg/kg). The experiment had a completely randomized design with three replications in pots of 2 kg soils. One brake fern seedling (approximately 7.5 cm tall) was transplanted to each pot and grown for 6 months. Recently fully mature leaf samples were collected and analyzed for As every month starting on the 2nd month after transplanting.

Results

Total As concentration in some soils, sediments, and stream waters of Hawaii

Our limited data (Table 1) suggest the followings: (1) As levels in Hawaii soils are quite variable, ranging from 15 to 950 mg/kg. (2) Observed elevated As levels in some stream waters are likely related to As-impacted soils. (3) Andisols seem to contain more total As than the other soil orders, perhaps because of high As sorption capacity of amorphous Al and Fe oxides that are predominant in the Andisols, and where sugarcane used to be grown and arsenical herbicides applied.

Table 1. Total As levels in soils, sediments, and stream waters in Hawaii.

Total As mg/kg			Soil Order			Sediment	Water
	Andisol (7 series)	Inceptisol (2)	Mollisol (1)	Oxisol (6)	Ultisol (11)	(3)	mg/L (4)
Range	25-950	15-67	55	15-133	37-84	12-45	0.080-0.005
Mean	163	41	55	72	60	29	0.029

Arsenic fractionation and chemical reactions in Hawaii soils

Table 2 presents different As fractions in two mineralogically different soils of Hawaii. The Olaa Andisol has 10.0% organic carbon (OC), and is X-ray amorphous, whereas the Lihue Oxisol has 1.5% OC and over 50% kaolinite and crystalline Fe oxides (mainly hematite). These contrasting properties in part explain for the high total As (448 mg/kg) in the Andisol vs. 15.6 mg/kg in the Oxisol. The distribution patterns of As fractions in the two soils may also have serious environmental and health implications: The Andisol has only 0.5% total As as exchangeable, implying most of its As is not easily released to the solution nor become available to living organisms. On the other hand, nearly 25% of its As is associated with soil organic matter (SOM), suggesting that some As may be gradually released upon the oxidation of SOM. Another 30% of total As was associated with amorphous iron oxides (as extracted by ammonium oxalate) that may be subjected to redox conditions of the soil (Table 2).

Table 2. Arsenic fractions in an Andisol and an Oxisol of Hawaii.

As fraction, mg/kg	Andisol (Olaa Series)	Oxisol (Lehue Series)
$CaCl_2$ (exchangeable)	2.4 (0.54%)	2.77 (17.72%)
Na-Pyrophosphate (organic matter)	110.4 (24.62%)	1.34 (8.57%)
NH_4-Oxalate (amorphous Fe/Al oxides)	132.7 (29.59%)	2.18 (13.95%)
HNO_3 (recalcitrant)	202.9 (45.25%)	9.34 (59.75%)
Total	448.4 (100%)	15.63 (100%)

Desorption and sorption of As in Hawaii soils

Consistent with the different As fractions, As was desorbed (released) faster in the Oxisol (maximum desorption at cycle 3 or 4) than in the Andisol (maximum at cycle 5) (Figure 1). In general, it took at least 10 cycles to desorb soil As to levels below our detection (< 0.005 mg/L in solution or 0.05 mg/kg in soil). In contrast, the two soils can still sorb considerable amounts of As (Figure 1). For example, to maintain the 0.20 mg As/L in solution, it requires an addition of 220 mg As/kg to the Andisol and 150 mg/kg to the Oxisol (The action level of As in stream water in Hawaii is set at 0.19 mg/L). The sorption is much stronger (steeper slope) for the Andisol when As in the equilibrium solution is below 0.10 mg/L (Figure 1).

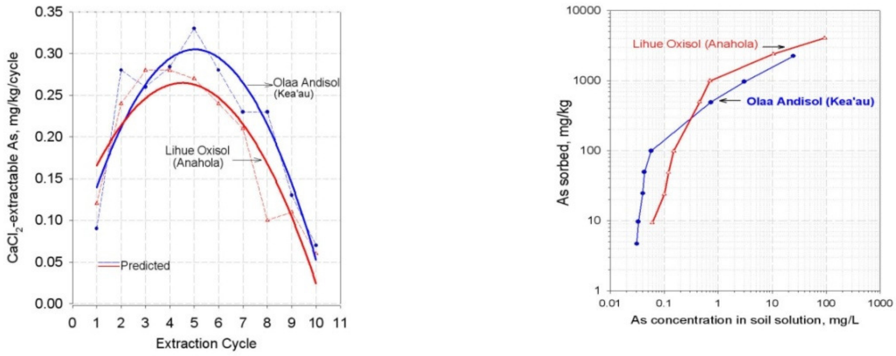

Figure 1. Desorption (left) and sorption of As in an Andisol and an Oxisol of Hawaii.

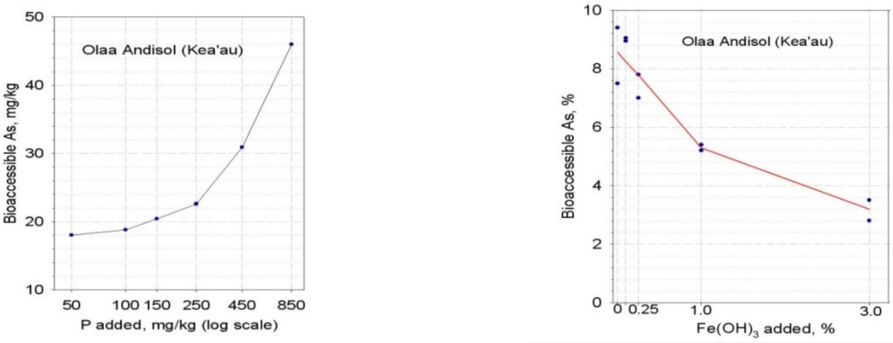

Figure 2. Effects of P fertilizer (left) and amorphous $Fe(OH)_3$ additions on HCl-extractable (bioaccessible) As in a high-As Andisol of Hawaii.

Effects of soil amendments on As bioaccessibility

Adding P fertilizer to the high-As Andisol releases significant amounts of As (Figure 2). For example, bioaccessible As increased from 18 to 31 mg/kg when 450 mg P/kg as $Ca(H_2PO_4)_2$ was added. On the other hand, adding colloidal $Fe(OH)_3$ decreases bioaccessible As markedly. For example, 1% $Fe(OH)_3$ reduced bioaccessible As from 9% of total As to 5% (Figure 2).

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

Brake ferns grown on the high As Andisol had between 500 and 1000 mg As/kg in their leaves. The above-ground biomass produced was between 30 and 70 g/pot dry weight for a 3-month growth; and the compost treatment provided the best growth whereas the $Fe(OH)_3$ treatment the least (Figure 3). However, As concentration in ferns grown on the low-As Oxisol was only 30-50 mg/kg, suggesting As uptake depends on soil As, or perhaps the ratio of As bioaccumulation (As concentration in leaf/As concentration in soil) is rather constant (at approximately 2.5:1 of plant As:soil As) for this fern.

Figure 3. Chinese brake fern (*Pteris vittata* L.) grown on an Andisol of Hawaii treated with $Fe(OH)_3$, P fertilizer or compost (3 weeks after transplanting).

Conclusion

Chronic exposure to As often manifests as hyperpigmentation and hyperkeratosis, particularly in hands and feet. Skin and other types of cancer may follow. Past use of arsenical pesticides has resulted in elevated levels of As in many areas of Hawaii. High proportions of total soil As, however, are associated with iron oxides, organic matter, or are recalcitrant, thus not bioavailable in the short term. On the other hand, phosphate fertilization or compost application could release more As into the soil solution; and Chinese brake fern (*Pteris vittata* L.) could be used to extract soil As for remediation purpose.

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