

Approaches to Reduce Bioaccessible As in Hawaii Soils

William Cutler (Environmental Resources Management and University of Hawaii,
Honolulu, Hawaii, USA, william.cutler@erm.com)

Nguyen Hue and Maria E. Ortiz-Escobar (University of Hawaii, Honolulu, Hawaii, USA)

Todd Martin (Integral Consulting, Broomfield, Colorado, USA)

ABSTRACT: Historical application of arsenical pesticides has resulted in elevated levels of arsenic (As) in surface soils in many historic sugar cane areas in Hawaii. The authors have investigated the arsenic (As) soil chemistry of an Andisol with total As levels of 200 to 900 mg/kg. Hawaiian soils contain significant iron and aluminum oxyhydroxides that have a strong affinity to adsorb As oxyanions, resulting in low As bioaccessibility from 5 to 20 percent of total As, as measured by *in vitro* extraction procedures. There is growing acceptance that only a fraction of total soil arsenic contributes to potential human health risks from exposure to As-containing soils, and therefore the bioaccessible fraction should be considered in risk assessments and addressed by any remedial solutions. Batch leaching tests utilizing a weak salt solution (0.01 molar CaCl₂) failed to desorb any soil As, attesting to its strongly adsorbed state. However, the presence of only 2 mg/L of dissolved phosphate in the extractant stimulated the desorption of As. Soils were amended with colloidal ferric hydroxide (Fe(OH)₃) at varying doses, resulting in significant reduction of bioaccessible As. The authors suggest that amending soils with Fe(OH)₃ could be an effective *in situ* or *ex situ* remedial alternative to traditional capping or removal remedies.

INTRODUCTION

Arsenic is a naturally occurring element in rocks, soils, sediments, and groundwater. Anthropogenic activities, such as the application of arsenical pesticides, can result in soil As levels above natural “background” levels. In surface soils, As typically occurs in an inorganic state as an oxyanion species. Under oxidizing conditions arsenate (As^V) is the prevalent form, whereas, arsenite (As^{III}) is present under reducing conditions and is more toxic and mobile than arsenate (Meharg and Hartley-Whitaker, 2002).

Arsenic Soil Chemistry. Arsenic chemistry and mobility in soils is dependent on soil solution chemistry (primarily pH and redox conditions), solids composition, As-bearing phases, adsorption and desorption, biological transformations and volatilization (Sadiq, 1997). Soil organic matter (SOM) probably has a limited role in sequestering inorganic As, since the As oxyanions are not strongly sorbed to the net negatively charged SOM. SOM may indirectly affect As^V chemistry by causing more reducing conditions and mediating the reduction of As^V to As^{III} (Goh and Lim, 2004). As oxyanions have a strong adsorption affinity for metal oxyhydroxides of iron, aluminum, and manganese; iron hydroxides being the most common in Hawaiian soils. Adsorption of As oxyanions onto soil particles, and partitioning between the soil solid and soil solution phases, is primarily controlled by soil pH, redox, and iron oxide content (Elkhatib et al., 1984; Jian et al., 2005).

Bioavailability and Bioaccessibility. There is a growing acceptance that only a fraction of total soil As contributes to potential health risks from ingestion of As-containing soils. *In vivo* animal studies are used to determine the bioavailability of toxic compounds, including As; whereas *in vitro* laboratory tests have been developed to provide a cost-effective surrogate method of assessing bioavailability (Ruby, et al., 1996). These *in vitro* tests provide a measure of “bioaccessible” As, the fraction of total As that partitions from the soil to the extractant solution during the *in vitro* test. A growing body of work in comparing *in vivo* and *in vitro* test methods is providing validation of the *in vitro* test methods (Basta et al., 2002).

Study Objectives. The primary objectives of this study are to:

- Evaluate As desorption to a simulated soil solution to assess the potential for impacts to groundwater,
- Determine As bioaccessibility for evaluation of potential human health risk,
- Determine whether known oxyanion sorbent amendments, $\text{Fe}(\text{OH})_3$, reduce As bioaccessibility, and
- Develop conceptual remedial strategies to address elevated bioaccessible As in Hawaiian soils.

FIELD AND LABORATORY METHODS

Site Location. The study site is located near the town of Kea’au on the island of Hawaii, in an area of historic sugar cane production (Figure 1). In addition to sugar cane planting,

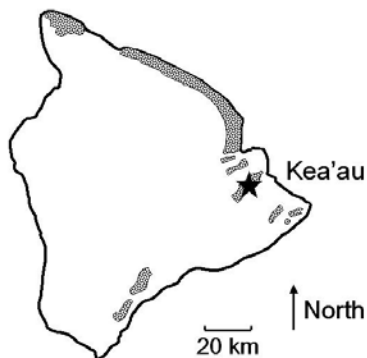


FIGURE 1. Sugar cane plantings (shaded) on island of Hawaii in 1937 (Ripperton et al. 1939).

a portion of the site was developed as a plantation worker camp with housing and community gardens. The site is currently vacant and highly vegetated, and contains soil As levels from 200 to 900 mg/kg. Arsenical pesticides were widely used on sugar cane in Hawaii during the first half of the 20th century, and elevated levels at the subject site are attributed to this activity.

Soil Sampling. Shallow soils were collected from 3 to 6 inches (7.5 to 15 cm) below ground surface. A primary sampling event in March 2005 collected random grab samples for general characterization of soil properties and chemical impacts. A second sampling event in August 2005 collected multi-increment samples from

one- to two-acre “decision units” to support human health risk assessment and remedy selection. Multi-increment samples consisted of composite samples of 35 to 40 discrete sample increments from each decision unit.

Soil Preparation and Subsampling. Samples were air dried and sieved into two grain-size fractions: a <2 mm “soil fraction” and a <0.25 mm (<250 μm) “fine fraction”.

Chemical concentrations in the fine fraction are used for *in vitro* bioaccessibility testing (Ruby et al., 1996) and associated human health risk assessments, since fine soil particles are most likely to be incidentally ingested or inhaled. Multi-increment samples for risk assessment purposes were prepared as per grab samples, however the entire bulk sample was consumed to create a representative fine fraction sample. A rotary riffler splitter was used to prepare replicate subsamples for bioaccessible As and Fe(OH)₃ soil amendment studies.

Soil Characterization. The soil fraction and fine fraction were characterized for physical and chemical properties, using a variety of methods. General properties such as moisture, pH and grain size distributions were performed at the University of Hawaii. Elemental analysis and total organic carbon (TOC) analysis were performed by standard EPA methods at a commercial laboratory in Portland, Oregon. Mineralogical analyses by X-ray diffraction (XRD), scanning electron micrography (SEM) and electron microprobe were performed by a commercial laboratory in Seattle, Washington.

Batch Desorption Tests. Batch desorption tests (extractions) were employed to determine the potential mobility of soil As in a simulated soil solution and in the presence of low levels of dissolved phosphate. The extractant fluid utilized was a weak salt solution of CaCl₂ (0.01 M), intended to mimic a typical soil solution in Hawaiian soils in terms of ionic strength and composition (Fox, 1981). A salt solution extractant has been employed as the initial step in sequential extraction techniques to define the weakly adsorbed arsenic pool that might readily partition between the soil solid and soil solution phases (Keon et al., 2001). This weak salt solution extraction test estimates the potential for soil As to partition to the soil solution, migrate downward within the soil profile and potentially impact groundwater. The same CaCl₂ solution was further amended with orthophosphate (2 mg/kg P-equivalent KH₂PO₄) to observe the potential competitive displacement of arsenate by phosphate that has been well documented in the literature (Hingston et al., 1971; Livesay and Huang, 1981; Martin and Ruby, 2003).

Extractions were conducted using a 1:100 soil:solution ratio in 30 ml polycarbonate centrifuge tubes at 22°C. Centrifuge tubes were pre-cleaned with nitric acid (HNO₃) wash and distilled water rinse. Extractions were performed in triplicate with reagent blanks (0.01 molar CaCl₂ solution without soil) as controls, and run for 24-48 hours with periodic shaking. Soil samples were subjected to three successive extractions using the identical CaCl₂ extractant to observe As desorption effects. Aliquots of extractant were collected after centrifuging and filtering (0.45µm) in clean polyethylene vials, acidified to approximately pH 2 with HNO₃, and analyzed for dissolved As by trace ICP/MS (EPA methods 3050B/200.8).

An initial set of extractions varied the pH of the soil/CaCl₂ solution, titrating with NaOH and HCl, to one pH standard unit above and below the natural pH of the un-adjusted soil/CaCl₂ solution pH (with un-adjusted sample for control). A second set of extractions was performed with the addition of dissolved orthophosphate in the CaCl₂ extractant to observe the competitive effects of the phosphate oxyanion on selective displacement of As. A suite of sequential extractions, similar to those described above for the initial pH adjustment study, were conducted without pH adjustment using an un-amended CaCl₂ extractant as a control and one with 2 mg/l dissolved P at natural soil

slurry pH of approximately 6.5-6.9. Three sequential extractions were performed for each sample, with triplicate replication.

***In Vitro* Bioaccessible Metals Testing.** An *in vitro* method for determination of bioaccessible As and lead (Pb) has been developed by several researchers (Ruby 1996; Drexler 2006) to simulate As and Pb removal by the human digestive system upon ingestion of soils. The method uses the soil fine fraction (<0.25 mm) that would most likely stick to the hands and be incidentally ingested. This batch extraction technique uses a glycine-buffered HCl solution at pH 1.5 for a one-hour duration at 37°C (human body temperature) to simulate the stomach digestion process. *In vitro* bioaccessibility tests were run at the University of Colorado, Boulder. The soil:extractant ratio is 1:100, typically using 1 g of soil to 100 mL of extractant. Splits of a soil sample were analyzed for total As by standard EPA methods 3050B/6020 (ICP/MS), and the extracts were analyzed for dissolved (bioaccessible) As by method 6020. A comparison of dissolved to total soil As provided the percentage of bioaccessible As.

Bioaccessible As in Iron Hydroxide Amended Soils. Arsenic treatment of drinking water and wastewater commonly employs adsorption technologies, such as granular ferric hydroxide materials (Banerjee et al., 1999). In addition, several researchers (Martin and Ruby, 2003) have indicated that As adsorption is feasible in a soil or solid waste matrix using iron hydroxide amendments. Fine fraction soils from the Kea'au site were amended with a range of reagent-grade colloidal ferric hydroxide (Fe(OH)₃) obtained from a chemical manufacturer. Starting with a non-amended control, the dosing rates ranged from 10⁻³ weight ratio Fe(OH)₃:soil (0.1 weight percent) to 10^{-1.5} weight ratio (3 weight percent), in 0.5 order of magnitude increments. The colloidal Fe(OH)₃ was added to soil samples at appropriate dosing, and deionized water was added to allow complete hand mixing/stirring of the sample. Amended samples were air dried for one month prior to duplicate subsampling and *in vitro* bioaccessible As analysis.

RESULTS AND DISCUSSION

Soil Characterization. The subject Andisol is an immature, stoney, organic-rich, light to dark grey soil with high organic content, low bulk density, and high field capacity. The soil is the weathering product of basaltic lava parent rocks in the wet tropical climate of the eastern island of Hawaii. The significant total soil organic carbon content of the site soils, up to 20 weight percent in the fine fraction, affects aspects of color (dark grey), bulk density (approximately 0.5 g/cm³) and field capacity (approximately 100 percent) in these soils. Table 1 shows selected chemical properties including major elements and several trace metals.

Coarse materials >2 mm constituted 30% to 50% of bulk samples, and consisted of fresh to weathered fragments of basaltic lava (many with small visible olivine phenocrysts). Only 2% to 3% of the bulk mass was in the fine fraction (<0.25 mm) size range.

TABLE 1. Chemical characterization of soil and fine fractions of Kea'au Andisol

Particle size	Major Elements & TOC (weight %)							Trace Elements (mg/kg)			pH
	Al	Ca	Fe	Mg	Mn	P	TOC	As	Pb	Zn	
Soil Fraction (<2 mm)	2.27	0.60	6.15	3.98	0.12	0.16	14.1	232	282	670	6.5-6.7
Fine Fraction (<0.25 mm)	2.62	0.85	4.48	1.81	0.07	0.24	21.8	272	340	823	-

Naturally-occurring background levels of As and Pb in Hawaiian soils are general less than 20 mg/kg. The elevated levels of As (and possibly Pb) in the subject soils are believed to be anthropogenic in origin, the result of the application of arsenical pesticide usage related to the sugar cane production ubiquitous to the area in the early to mid 1900's (Hanson, 1962).

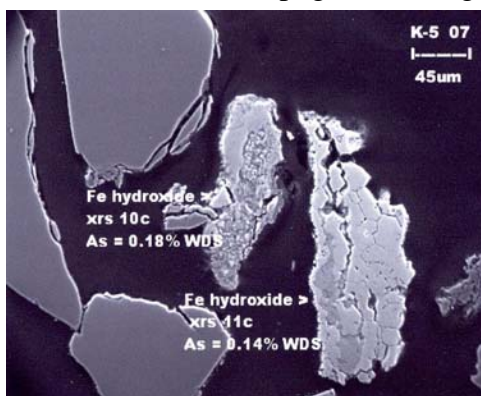


FIGURE 2. SEM of porous iron hydroxide grains with 0.14 and 0.18 weight percent As at selected electron microprobe targets.

Soil Mineralogy and As Association. X-ray diffraction (XRD) patterns of fine fraction soils showed abundant amorphous (poor crystallinity) grains. SEM and electron microprobe spectral analysis identified elevated As levels in association with amorphous iron hydroxides, with As levels up to 0.22 weight percent (2200 mg/kg). No detectable As was found in association with other mineral phases. SEM of the iron hydroxide mineral grains (Figure 2) shows high microporosity (and surface area), and authigenic origin (micro-laminar encrustation and inclusion of other mineral grains).

Batch Desorption Tests. The batch desorption studies using a 0.01M CaCl₂ extractant at a range of pH conditions showed no As in sample extracts above blank controls (all <8 μg/l dissolved As). Therefore, the results suggest that under field conditions As desorption by naturally occurring pH shifts due to precipitation, organic material decomposition, or mineral weathering are unlikely to release As from soils into the soil solution.

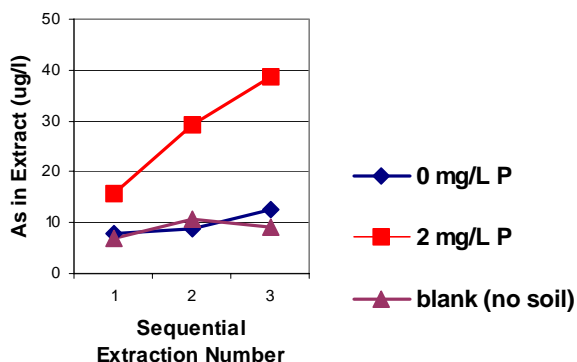


FIGURE 3. Effect of dissolved phosphate on competitive desorption of As

In the presence of 2 mg/L dissolved P, soil As was released into the extractant, with more As released during each successive sequential extraction (Figure 3).

Competitive displacement of As by phosphate is well documented in the literature (Goh and Lim, 2004;

Martin and Ruby, 2003). In addition, the extraction procedures developed by Keon et al. (2001), use a phosphate solution to measure the strongly adsorbed As pool (albeit a much more concentrated P solution), after a prior $MgCl_2$ salt extraction to defined the loosely adsorbed As pool. In the three sequential extractions performed on the Kea'au fine fraction soil, the cumulative As desorption from the soil was approximately 4 mg/kg (100x the extractant concentration due to 100:1 extractant:soil ratio), representing only about 1.5% of the measured total soil As. Over three successive extractions (see Figure 3) total As extracted increased in each successive extraction step; further As desorption is expected if additional sequential extraction were to be performed.

Bioaccessible Arsenic. Fine fraction soils from various decision units were analyzed for total and bioaccessible As (Figure 4). Bioaccessible As levels ranged from 8.7 to 21.9 percent of total As, with a clear increase in bioaccessible As with increasing total As in the soils.

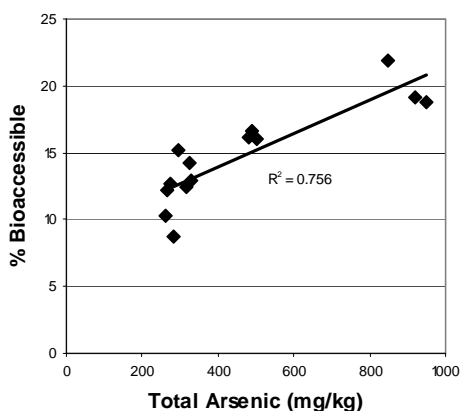


FIGURE 4. Bioaccessible versus total As.

bioaccessible As from around 9 to 5.5 percent of total soil As (Figure 5). High amendment dosing, at 3 weight percent $Fe(OH)_3$ reduced bioaccessible As to approximately 3% of total soil As, a three-fold reduction in As bioaccessibility. The result strongly suggests that As has migrated from weaker native soil adsorption sites to stronger adsorption sites on the amended $Fe(OH)_3$. Further work is ongoing to understand the mechanisms of As sorption, and on the stability of $Fe(OH)_3$ amended soils over a range of geochemical conditions.

CONCLUSIONS

Our studies of an As-impacted Andisol from Kea'au, Hawaii show 200 to 900

in the soils. This trend indicates decreasing sorption capacity at higher contaminant levels, where progressively weaker sorption binding sites are being accessed as the As loading increases. Despite the relatively low percent bioaccessibility, bioaccessible As levels ranges from 30 to 180 mg/kg. The higher end of this range require remedial measures to address the potential human health risks from soil exposure.

Arsenic Bioaccessibility in Iron Hydroxide Amended Soils. Amendments of colloidal $Fe(OH)_3$ clearly reduce the bioaccessible fraction of As in the fine fraction subject soils.

Addition of 1 weight percent $Fe(OH)_3$ reduced

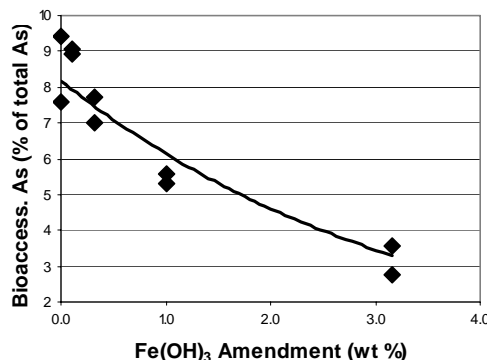


FIGURE 5. Effect of iron hydroxide amendments on As bioaccessibility

mg/kg of total soil As, primarily in association with the amorphous iron hydroxide mineral fraction. Batch desorption tests indicate very low potential for As desorption into the soil solution; consequently groundwater impacts from these soils are unlikely to occur under typical field conditions. Phosphate in solution causes the competitive displacement of As, and application of phosphate-based fertilizers to these soils could cause As release. Bioaccessible As represents 5 to 20 percent of total As, as determined using an *in vitro* extraction technique. Ferric hydroxide amendments significantly reduce bioaccessible As, with up to three-fold bioaccessibility reduction observed with 3 weight percent Fe(OH)₃ addition.

A hierarchy of remedial solutions for elevated bioaccessible As in Hawaiian soils begins with land-use controls and capping/containment as the most cost effective solutions, but not always feasible or desirable. Limited landfill space and associated high disposal costs make innovative alternatives appealing. Iron hydroxide amendments to reduce bioaccessible As could be employed *in situ* or *ex situ* as an alternative to soil removal remedies.

ACKNOWLEDGEMENTS

The authors would like to thank the Hawaii Department of Health for their financial and technical support of the project, in particular John Peard, Melody Calisay, Roger Brewer, Davis Bernstein and Clarence Callahan. Dr. John Drexler at the University of Colorado, Boulder generously provided *in vitro* bioaccessible arsenic testing to the project, and Bart Cannon conducted mineralogical analyses. Finally, the laboratory support of Aminata Diarra, Gaoussou Diarra and Hamidou Konare is greatly appreciated.

REFERENCES

- Banerjee K., R.P. Helwick, and S.K. Gupta. 1999. "A Treatment Process for Removal of Mixed Inorganic and Organic Arsenic Species from Groundwater." *Environ. Progress*. 18(4) 280-284.
- Basta, N.T, R.R.Rodriguez, and S.W. Casteel. 2002. "Bioavailability and Risk of Arsenic Exposure by the Soil Ingestion Pathway." In: W.T. Frankenberger, Jr. (Ed.), *Environmental Chemistry of Arsenic*. pp. 117-139. Marcel Dekker, New York.
- Drexler, J. 2006. "The In Vitro Method, Relative Bioavailability Leaching Procedure, Standard Operating Procedure." <http://www.colorado.edu/geolsci/legs/invitrol.html>
- Elkhatib, E.A.; O.L. Bennet, and R.J. Wright. 1984. "Kinetics of Arsenite Sorption in Soils." *Soil Science Society of America Journal*. 48:758-762.
- Fox, R. L. 1981. "External Phosphorus Requirements of Crops." In: *Chemistry in the Soil Environment*. Special Publ. No. 40, pp. 223-239. Soil Science Society of America. Madison, WI.
- Goh, K.H. and T.T. Lim. 2004. "Geochemistry of Inorganic Arsenic and Selenium in a Tropical Soil: Effect of Reaction Time, pH, and Competitive Anions on Arsenic and Selenium Adsorption." *Chemosphere*. 55:849-859.
- Hanson, N. 1962. "Weed Control Practices and Research for Sugar Cane in Hawaii." Journal Series of the Experimental Station, Hawaiian Sugar Planter's Association. *Weeds* 10(3):192-200.

- Hingston, F.J., A.M. Posner, and J.P. Quirk. 1971. "Competitive Adsorption of Negatively Charged Ligands on Oxide Surfaces." *Disc. Farada Soc.* 52:234-342.
- Jian, W., Zhang, S., Shan, X., Feng, M., Zhu, Y.G. and R.G. McLaren. 2005. "Adsorption of Arsenate on Soils: Part 2. Modeling the Relationship between Adsorption Capacity and Soil Physicochemical Properties using 16 Chinese Soils." *Environmental Pollution*. 138:285-289.
- Keon, N.E., C.H. Swartz, D.J. Brabander, C. Harvey, and H.F. Hemond. 2001. "Validation of an Arsenic Sequential Extraction Method for Evaluating Mobility in Sediments." *Environ. Sci. Technol.* 35:2778-2784.
- Livesay, N.T. and P.M. Huang. 1981. "Adsorption of Arsenate by Soil and its Relation to Chemical Properties and Anions." *Soil Science*. 131:88-94.
- Martin, T.A. and M.V. Ruby. 2003. "In Situ Remediation of Arsenic in Contaminated Soils." *Remediation*. Winter 2003 issue, pp. 21-32.
- Meharg, A. A. and J. Hartley-Whitaker. 2002. "Arsenic Uptake and Metabolism in Arsenic Resistant and Non-resistant Plant Species." *New Phytologist*. 154:29-43.
- Ripperton, J.C., J.W. Coulter and R.H. Moulzau. 1939. "An Historic Inventory of the Physical, Social, Economic & Industrial Resources of the Territory of Hawaii" *First Progress Report*. Territorial Planning Board.
- Ruby, M. V., A. Davis, R. Schoof, S. Eberle and C.M. Sellstone. 1996. Estimation of Lead and Arsenic Bioavailability using a Physiologically Based Extraction Test. *Environ. Sci. Technol.* 30:422-430.
- Sadiq, M. 1997. "Arsenic Chemistry in Soils: an Overview of Thermodynamic Predictions and Field Observations." *Water, Air and Soil Pollution*. 93:117-136.