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Bioaccessible Arsenic in Soils of Former Sugar Cane Plantations, Island of Hawaii

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12 ABSTRACT (PURPOSE, METHOD, RESULTS, CONCLUSIONS)

Arsenical herbicides were used extensively for emergent weed control in Hawaiian sugar cane cultivation from 1913 to about 1950. As a result, surface soil arsenic concentrations average 280 mg kg^{-1} across more than 60 km^2 of former sugar plantation land in the eastern portion of the Island of Hawaii. This study was conducted to elucidate the relationship between soil properties and arsenic bioaccessibility in the iron-rich volcanic soils. Soils are predominantly Andisols, formed by weathering of basaltic lava and tephra, with pedogenic solid phases consisting of short-range order iron oxyhydroxides, allophane-like aluminosilicates, and metal-humus compounds. These reactive solid phases strongly adsorb oxyanions, such as phosphate and arsenite/arsenate. High arsenic sorption capacity limits desorption and vertical migration within the soil column and prevents contamination of the underlying groundwater aquifer, despite high arsenic loading and precipitation rates. *In vitro* arsenic bioaccessibility, as measured by the SBRC gastric-phase test, ranges from 2% to 35% and averages 9% of total arsenic. Bioaccessible arsenic is higher in less weathered soils (Udifolists, Typic and Lithic Hydrudands) and lower in more weathered ash-dominant soils (Acrudoxic Hydrudands). Soil weathering indicators, such as reactive iron content, are strong predictors of arsenic bioaccessibility. Based on evidence from soil mineralogy, geochemistry and arsenic speciation, as well as limited soil arsenic bioavailability/bioaccessibility comparisons, risks to human health from direct contact (soil ingestion) are significantly reduced by low arsenic bioaccessibility. Nonetheless, some soils within former sugar cane cultivation areas contain bioaccessible arsenic concentrations exceeding Hawaii Department of Health risk-based action levels, and will require mitigating actions. Even higher levels of soil arsenic contamination have been identified at former pesticide storage and mixing areas, but are generally of localized extent.

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Abstract

Arsenical herbicides were used extensively for emergent weed control in Hawaiian sugar cane cultivation from 1913 to about 1950. As a result, surface soil arsenic concentrations average 280 mg kg^{-1} across more than 60 km^2 of former sugar plantation land in the eastern portion of the Island of Hawaii. This study was conducted to elucidate the relationship between soil properties and arsenic bioaccessibility in the iron-rich volcanic soils. Soils are predominantly Andisols, formed by weathering of basaltic lava and tephra, with pedogenic solid phases consisting of short-range order iron oxyhydroxides, allophane-like aluminosilicates, and metal-humus compounds. These reactive solid phases strongly adsorb oxyanions, such as phosphate and arsenite/arsenate. High arsenic sorption capacity limits desorption and vertical migration within the soil column and prevents contamination of the underlying groundwater aquifer, despite high arsenic loading and precipitation rates. *In vitro* arsenic bioaccessibility, as measured by the SBRC gastric-phase test, ranges from 2% to 35% and averages 9% of total arsenic. Bioaccessible arsenic is higher in less weathered soils (Udifolists, Typic and Lithic Hydrudands) and lower in more weathered ash-dominant soils (Acrudoxic Hydrudands). Soil weathering indicators, such as reactive iron content, are strong predictors of arsenic bioaccessibility. Based on evidence from soil mineralogy, geochemistry and arsenic speciation, as well as limited soil arsenic bioavailability/bioaccessibility comparisons, risks to human health from direct contact (soil ingestion) are significantly reduced by low arsenic bioaccessibility. Nonetheless, some soils within former sugar cane cultivation areas contain bioaccessible arsenic concentrations exceeding Hawaii Department of Health risk-based action levels, and will require mitigating actions. Even higher levels of soil arsenic contamination have been identified at former pesticide storage and mixing areas, but are generally of localized extent.

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Introduction

Problem Definition and Study Objectives

Arsenic contaminated soil is an emerging environmental issue in the State of Hawaii that complicates property transactions, hinders land development, and could present a human health risk under certain exposure settings. In 2006, the Hawaii Department of Health (HDOH) discovered arsenic contamination in the former sugar cane cultivated soils in the Puna district on the east side of east the Island of Hawaii (HDOH 2007a). A study carried out by HDOH, with the assistance of the US Centers for Disease Control and Prevention, did not identify health impacts to residents in the area and concluded that the primary exposure to inorganic arsenic was dietary (ATSDR and HDOH 2008). Arsenic contamination has subsequently been identified in former sugar cane fields on other Hawaiian islands, but in most cases the reported concentrations of arsenic in soil were lower than those observed in the eastern portion of the Island of Hawaii. The level of arsenic contamination on different former sugar cane plantation soils appears to vary widely depending on the period of plantation operation, frequency of herbicide use, application rates and methods, as well as other factors. Former pesticide mixing and storage areas located at many of the former plantations, where the release of arsenic to soil has occurred, exhibit the highest concentrations of arsenic contamination, far exceeding the average arsenic contamination levels in the surrounding fields.

The health risk posed by arsenic in soil, as well as other chemicals, may be evaluated in part by its bioavailability in incidentally ingested contaminated soil (USEPA 2007). Bioavailability describes the fraction of the chemical extracted from the soil in the digestive system and taken up in the bloodstream; and thus, is "available" to cause potential adverse health effects. Bioavailability is ideally estimated by *in vivo* laboratory tests, where small amounts of the soil with known chemical concentrations are fed to laboratory animals, and the fraction of uptake measured. The relative oral bioavailability of soil arsenic in animal models (e.g., monkey, juvenile swine, and mouse) for individual sites is highly variable and partly controlled by soil mineralogy and geochemical conditions (Roberts et al. 2007, Juhasz et al. 2007, Scheckel et al. 2009). While very useful, the expense and time required to carry out *in vivo* tests on a site-by-site basis make this method impractical for routine use in environmental investigations.

In vitro bioaccessibility assays, with proper validation, can be used as an alternative predictor of relative oral bioavailability of metal(loid)s (Ruby et al. 1996). In lieu of costly animal studies of relative arsenic bioavailability, various batch chemical extraction tests (*in vitro* tests) have been devised to estimate bioavailability of metals in soils, sediments and waste solids (Oomen et al. 2002, Juhasz et al. 2009). The arsenic extracted in *in vitro* tests is termed bioaccessible arsenic (Ruby et al. 1996). *In vitro* arsenic bioaccessibility (As_{IVBA}) may be a suitable predictor of relative arsenic bioavailability (USEPA 2007), particularly when validated by *in vivo* animal studies. The HDOH (2006, 2010) recommends use of As_{IVBA} in evaluation of potential human health risk and need for remedial action at sites with arsenic contaminated soil, and as a matter of policy, assumes 100% of bioaccessible arsenic is bioavailable.

This study evaluated the soil property and geochemical controls on arsenic bioaccessibility in iron-rich, volcanic soils of the easternmost island in the State of Hawaii, referred to as the "Island of Hawaii" or the "Big Island." The objectives of the current study were to determine: 1) the areal and vertical extent of arsenic in former sugar cane soils of the eastern portion of the Island of Hawaii, 2) the speciation of arsenic and its solid-phase associations, and 3) the degree of bioaccessibility and potential mobility of soil arsenic in these soils.

Study Area Description

Sugar cane cultivation was widespread in the eastern portion of the Island of Hawaii on the lower windward slopes of the Mauna Kea, Mauna Loa and Kilauea volcanoes from the mid-1800s until the late 1900s. Plantations were established where soil development was sufficient, below elevations of 600 m above mean sea level, with a mean annual temperature of 20.5°C and an annual rainfall of approximately 4,000 mm (Giambelluca et al. 2011). Two large plantations were established within the study area: the Waiakea Mill Company plantation near Hilo (1879 to 1947) and the Olaa Sugar Company (later called Puna Sugar Company) plantation (1900 to 1982) (Figure 1). Sugar cane cultivation reached its full historic extent by the 1920s (Territorial Planning Board 1939, Dorrance and Morgan 2000), extending across approximately 60 km^2 (6,000 hectares) within the study area. Current land use consists of commercial and residential (particularly in Hilo), diversified agriculture (papaya, macadamia nuts, and ornamentals), and fallow land.

Arsenical herbicides were first used in the State of Hawaii in 1913 (Larsen 1914a, 1914b). By the late 1940s, the widespread use of arsenical herbicides ceased, and was replaced by synthetic organic herbicide compounds (pentachlorophenol [PCP] and 2,4-dichlorophenoxyacetic acid [2,4-D]) (Hance 1948, Hanson 1959). Additional detail on historical arsenical herbicide use in Hawaii is provided in the supplemental information, including historical photographs of arsenical herbicide application techniques (Appendix Figure B.1).

Water for domestic consumption and irrigation in the study area is derived from groundwater, extracted from wells penetrating a basal aquifer system, classified as irreplaceable fresh water (<250 mg L^{-1} chlorides), with a high vulnerability to contamination (Mink and Lau 1993). To date, no arsenic has been reported (reporting limit of 2μg L^{-1}) in groundwater from public drinking water wells routinely tested within the boundaries of the former Olaa Sugar Plantation, or in any public drinking water wells in the State of Hawaii (HDOH 2009).

The Hawaiian Islands are a chain of volcanic islands formed from historic and ongoing basaltic eruptions. Basalt flows from Mauna Loa (Kau Basalt) and Kilauea (Puna Basalt) are composed dominantly of tholeiitic aa and pahoehoe flows, consisting of plagioclase, pyroxene, and olivine, with lesser amounts of magnetite, ilmenite, and apatite (Stearns and Macdonald 1946, Macdonald 1949). Tephra deposits, dominantly composed of ash and lapilli, are intercalated with basalt flows (Wolfe and Morris 1996).

Within the study area, elongated lava flows of Pleistocene and Holocene age trend northeast-southwest, originating from vent and fissure sources along the flanks of Mauna Loa. Holocene to recent flows from Kilauea are present in the southeast portion of the island, whereas older flows derived from Mauna Kea occur north of Hilo Bay along the Hamakua coast. Kau Basalt flows from Mauna Loa range in age from as young as 100 years to more than 11,000 years, whereas Puna Basalts from Kilauea range from recent to 3,000 years.

Soils have developed to varying degrees in emplaced basalt lava due to weathering of rock and accumulation of tephra, atmospheric dust and organic matter. Within the study area, soils of two taxonomic great groups are present: Hydrudands and Udifolists (Soil Survey Staff 2010). The spatial distribution of soil types is largely controlled by the underlying geology (see Appendix Figure B.2). Hydrudands are Andisols with a high water retention capacity (1,500 kPa water retention >100%), typically formed in part from volcanic ash. Acrudoxic Hydrudands are highly weathered with a low extractable base content, present as deep soils (>1 m thickness) in lava flows more than 10,000 years old. They are dominated by weathered ash components, and contain a small fraction of lithics (weathered basalt rock fragments). Acrudoxic Hydrudands have limited areal distribution within the study area, but are optimal soils for sugar cane cultivation because of their depth and ease of tillage. Typic and

Lithic Hydrudands are developed in lava flows that are approximately 3,000 to 10,000 years old, and are less weathered than Acrudoxic Hydrudands. They are generally <1 m in thickness, and have an appreciable lithic content (>35% rock fragments). The majority of the sugar cane cultivation in the study area occurred in Typic and Lithic Hydrudands. Udifolists are organic soils saturated with water less than 30 days per year. They represent initial soil formation on younger lava flows, generally less than 3,000 years old, and are not sufficiently developed to support sugar cane cultivation.

Andisols are characterized by andic properties in the fine fraction, including: low bulk density, high phosphate retention, and significant ammonium oxalate-extractable aluminum and iron (Soil Survey Staff 2006). Rapid weathering of parent mineral phases (glass, plagioclase, pyroxene and olivine) results in a pedogenic mineral assemblage of poorly crystalline, short-range order iron oxyhydroxides and aluminosilicates, which may persist for 1 million years or more. Formation of crystalline clays and sesquioxides occurs in Hawaii's oldest soils (Vitousek et al. 1997).

Materials and Methods

Soil samples were collected to support mapping of the spatial distribution of arsenic within the study area and for laboratory studies of soil properties, mineralogy, arsenic speciation, and bioaccessibility.

Sample Collection and Laboratory Preparation

Surface soils (0–20 cm depth) were collected from 134 locations within the study area Figure 2. Samples were composites of 6–8 discrete samples collected within an approximate 0.5 m × 0.5 m sample area. In addition to surface soil sampling, test pits (1–1.5 m depth) were excavated at several locations to assess vertical soil profiles. Soil samples were air dried and sieved to <2 mm grain size (soil fraction). A fine fraction (<250 μm) was prepared for *in vitro* analysis of arsenic. Soil Survey Staff (2004) uses the <2 mm grain size fraction for analysis of most soil properties, whereas the <250 μm fraction is used for evaluation of arsenic bioavailability and bioaccessibility. Subsamples for analysis were collected using a rotary riffler splitter or by multi-increment subsampling procedures (Gerlach and Nocerino 2003).

Mineralogical Assessment

Soil structure, mineralogy and relationship of parent and secondary solid phases were qualitatively evaluated using optical petrography on thin sections of air-dried soils. The fine silt and clay fraction (<10 μm particle sizes) was inspected by transmission electron microscopy (TEM) to determine secondary mineral phases based on morphology, internal structure and electron transmissivity.

Elemental Analysis

Elemental analysis of soils was performed using acid digestion/inductively coupled plasma (ICP) spectrometry and X-ray fluorescence (XRF) methods. Total elemental analysis was conducted on select soils, including samples from the vertical soil profiles, using a three acid digestion (similar to EPA Method 3052) with analysis by ICP optical emission spectrophotometry (ICPOES). Soil fraction (<2 mm) major element analysis was performed on fused soil powders using wave-dispersive XRF on the University of Hawaii Siemens 303 AS XRF spectrometer using a rhodium-target, end-window X-ray tube. Sample preparation followed methods similar to Norrish and Hutton (1977).

Various soil preparations were analyzed by energy-dispersive XRF using a Bruker Tracer III-V portable instrument utilizing a rhodium-target X-ray tube. Calibration for major and trace elements (Ca, Ti, Fe, Sr, and Zr) utilized a suite of Hawaiian soils (N = 20) analyzed by acid digestion and ICP. The presence of arsenic was determined by using site-specific standard reference materials (SS-SRMs), prepared by spiking study area soils with a sodium arsenate solution at a range of known arsenic concentrations.

In vitro bioaccessibility test method

A number of *in vitro* test methods have been developed to measure the bioaccessibility of metal(loid)s in solids, including the physiologically based extraction test (PBET, Ruby et al. 1993), the *in vitro* gastrointestinal model (IVG) (Rodriguez et al. 1999), the Unified BARGE Method (UBM) (Wragg et al. 2011) and the method developed by the Solubility/Bioavailability Research Consortium (SBRC) (Kelley et al. 2002, Drexler and Brattin 2007). These methods typically consist of a gastric phase extraction at low pH, followed sequentially by an intestinal phase at near neutral pH. For this study, the gastric phase of the SBRC test (SBRC-g) was selected for several reasons. A comparison study of PBET, IVG and SBRC methods for 20 soils from the study area (HDOH 2007b, Appendix Table C.1) showed that the SBRC-g *in vitro* method generated the highest $\mathrm{As_{IVBA}}$ values (percentage basis) of all methods. Therefore, SBRC-g is considered "conservative" relative to other gastric and intestinal phase *in vitro* testing methods, since it provided the highest estimate of $\mathrm{As_{IVBA}}$. Furthermore, Juhasz et al. (2009) determined that of the four *in vitro* methods (PBET, IVG, SBRC, and Deutsches Institut fur Normung e.V. [DIN 2000]) SBRC-g best predicted *in vivo* (juvenile swine) relative arsenic oral bioavailability for a suite of contaminated soils. A more recent study with a mouse model also supported using the SBRC-g method to estimate arsenic bioaccessibility (Bradham et al., 2011).

The SBRC-g *in vitro* test consists of batch extraction of 1 g of <250 μm air-dried (or oven-dried ≤40°C) soil by 100 mL of glycine-buffered HCl solution at pH 1.5, conducted in a 125 mL polyethylene bottle rotated in a 37°C water bath for 1 h. The <250 μm particle size fraction is considered the likely fraction to adhere to children's hands and be incidentally ingested (Duggan et al. 1985). A subsample of the extraction fluid is filtered through a 0.45 μm filter and analyzed for arsenic by ICPMS. Quality assurance/quality control procedures include blanks (raw extractant, no soil), blank spikes (extractant with arsenic spike, no soil), matrix spikes (soil spiked with arsenic), duplicate samples and control soil analyses (Drexler and Brattin 2007). A second aliquot of soil is evaluated for $\mathrm{As_{TOT}}$ using acid digestion, such as EPA method 3050B (hot plate $\mathrm{HNO_3}$-HCl), 3051A (microwave $\mathrm{HNO_3}$-HCl) or 3052 (microwave $\mathrm{HNO_3}$-HCl-HF), followed by ICPMS analysis of the acid extract. The percentage of bioaccessible arsenic is the mass of dissolved arsenic in the *in vitro* extract divided by mass of $\mathrm{As_{TOT}}$ in the test soil times 100 (Eq. 1). $\mathrm{As_{IVBA}}$ may be reported in concentration form as the mass of dissolved arsenic in the *in vitro* extract divided by the mass of the test soil (Eq. 2).

$$\mathrm{As_{IVBA}}(\%) = \frac{\textit{In vitro}\ \mathrm{As\,(mg)}}{\mathrm{Total\ As\ in\,soil\,(mg)}} \times 100 \qquad (1)$$

$$\mathrm{As_{IVBA}}\left(\mathrm{mg\ kg^{-1}}\right) = \frac{\textit{In vitro}\ \mathrm{As\,(mg)}}{\mathrm{Soil\,(kg)}} \qquad (2)$$

Arsenic Speciation

Soil arsenic speciation was determined by X-ray absorption near-edge structure (XANES) analysis for Typic Hydrudands, which were collected and kept field moist under a nitrogen atmosphere, frozen, and transported to the Stanford Synchrotron Radiation Laboratory (SSRL) for evaluation as described in Root et al. (2007). At SSRL, samples were transferred to Kapton tape in an $\mathrm{N_2}$ glovebox. Arsenic K-edge spectra was collected on SSRL beamline 11-2 at a beam energy of 80–100 mA, using a Ge detector and Si(220) monochromator crystal, with samples held in a liquid-He cryostat (5–20°K). Scans were processed (averaging and background corrections) using SixPACK software (Webb 2009) and normalized in spreadsheet software. Xanes spectra for study soil were compared to standard spectra from

Meharg et al. (2008) for arsenic species identification.

Targeted Dissolution of Ferric Iron Substrate

Reactive iron content was determined using targeted chemical extractions. The term "reactive" describes the fraction of an element that is extracted from soil by one of several chemical extraction tests designed to dissolve predominantly pedogenic (secondary) solid phase materials, which tend to be reactive toward sorption of oxyanions such as arsenite/arsenate and phosphate. Reactive iron was determined by two extraction methods, selected for their efficacy in quantifying specific mineral phases. The first consisted of extraction with 1M hydroxylamine hydrochloride (HAH) in 25% acetic acid in accordance with the method of Chester and Hughes (1967) as modified by Poulton and Canfield (2005). Approximately 100 mg of finely ground soil was placed in a 15 mL polyethylene centrifuge tube with 10 mL of extractant and shaken continuously for 48 h. The second reactive iron extraction method utilized dithionite in a pH 4.8 buffer of 0.35M acetic acid and 0.2M sodium citrate, per the method of Raiswell et al. (1994) as modified by Poulton and Canfield (2005). Approximately 80 mg of fine ground soil was extracted in 12 mL of citrate-dithionite (CD) solution in a 15 mL polyethylene centrifuge tube with continuous shaking over 2 h. For both extraction methods, at the end of the test duration, tubes were centrifuged for 5 min at 2,000 g and the supernatant was decanted and filtered through a 0.45 μm polypropylene filter. Filtrate was analyzed for iron by ICPOES. Phosphorus was analyzed in CD extracts to measure the fraction associated with the pedogenic iron phases.

Poulton and Canfield (2005) compared the efficacy of various targeted extraction techniques for selective dissolution of common iron oxyhydroxide/oxide minerals. Their work (see Appendix Table C.2) demonstrated that the CD method provided the most complete dissolution of secondary iron minerals (ferrihydrite, lepidocrocite, goethite, and hematite), whereas HAH dissolved only the most reactive iron forms (i.e., ferrihydrite and lepidocrocite).

Results and Discussion

Mineralogy

The fine silt and clay fraction (<10 μm) of Ap and Bw horizons of Typic Hydrudands was examined by TEM to identify dominant secondary solid phases based on surface morphology, internal microstructure and electron transmissivity (Figure 3). The dominant solid-phase materials observed were finely crystalline iron oxyhydroxides (ferrihydrite, goethite), aluminosilicates (allophane and imogolite), and non-crystalline gel materials. Less abundant phases included layer silicates (halloysite, smectite), opaline silica, and partially weathered volcanic glass. In general, short-range order materials—ferrihydrite, allophane-like materials and gels—dominated the humus-rich shallower Ap horizons. More crystalline mineral phases—goethite, imogolite and layer silicates (halloysite, smectite)—were observed in the deeper Bw horizon soils, along with significant quantities of short-range order phases. The increased crystallinity of the solid phases in the deeper/older soils is believed to be the result of less humus impeding the crystal arrangement and more time for the crystal growth (Schwertmann 1988). These findings are consistent with those reported by other researchers of volcanic-ash soils (Dahlgren et al. 1993, Wada and Higashi 1976).

Major Element Content

Major element composition of soils within the study area is variable, and related to the age, provenance, and weathering history of parent volcanic materials. The degree of soil weathering can be inferred from deviations of elemental compositions from parent rock compositions provided by Wolfe and Morris (1996) and Sherrod et al. (2007). Weathering processes modify the bulk elemental composition of the soil. Certain elements tend to accumulate as soils weather, whereas others are depleted. Of the major elements sourced by the parent basalt rock, aluminum, titanium, manganese, and iron accumulate, while silicon, sodium, and calcium are depleted (Table 1, Cutler 2011).

The ratio of a depleting to an accumulating element provides a useful indicator of the degree of volcanic soil weathering, and is more pronounced than changes observed for single elements. In Udifolists and Hydrudands of the study area, the Ca/Ti ratio decreases substantially with progressive soil weathering, and shows a strong inverse non-linear relationship with total iron content, which increases as soils weather (Figure 4).

Iron in the parent rock of the study area averages 87 g kg^{-1}. Incipient soils formed on basalt (Udifolists), are slightly enriched in iron at about 94 g kg^{-1} (concentration in mineral solids after furnace combustion, which removes all water and organic compounds). In more weathered Typic and Lithic Hydrudands, iron averages 130 g kg^{-1}, almost twice the basalt content, and in highly weathered Acrudoxic Hydrudands averages 220 g kg^{-1}, approximately three times the basalt concentration.

Arsenic Speciation and Association with Solid Phases

Arsenic in soil, originating as an aqueous sodium arsenite solution sprayed on emergent weeds and soil (incidental overspray), is expected to strongly adsorb to secondary (pedogenic) solid phases in volcanic ash derived Andisols, consisting of amorphous to finely crystalline iron oxyhydroxides, aluminosilicates, and metal-humus compounds. Although these phases tend to form soil aggregates, they are dominantly found in the finest soil particle size fractions. A field-moist Typic Hydrudands from the Keaau area was separated into particle size fractions by wet sieving, then air dried and analyzed for As_{TOT} by acid digestion (EPA method 3050B) and ICPMS. Results show more than ten times As_{TOT} enrichment in the finest sieved fraction (<74 μm, passing through a 200 mesh sieve) as compared to the 0.5 to 2.0 mm size fractions. It is likely that arsenic is further enriched in the study soils in even finer particle size fractions, which are dominated by poorly crystalline pedogenic phases that strongly sorb arsenic. Smith et al. (2009) found significant arsenic (and iron) enrichment in the finest soil fraction (<2.5 μm) of Australian study soils, coincident with increased arsenic bioaccessibility (percentage basis). We have not evaluated arsenic bioaccessibility in various grain-size fractions, and do not know whether the findings of Smith et al. (2009) apply to arsenic-contaminated Hawaiian Andisols.

Solid-phase associations of arsenic in the study soils were examined by electron microprobe WDS analysis (Cutler 2011). Two dominant end member materials containing arsenic were identified as iron oxides and aluminosilicates. A cross-plot of arsenic content versus Fe/Fe+Al (molar basis) showed a general pattern of higher arsenic content in the more iron-rich solid-phase materials. Arsenic is known to adsorb to short-range order iron oxyhydroxides (such as ferrihydrite) (Sadiq 1995) and aluminosilicates (allophane and imogolite) (Gustafsson et al. 1998). Within the Hydrudands of this study, arsenic shows a general preference for binding to iron-rich phases, however, arsenic binding to aluminosilicate phases may also be occurring.

Arsenic in most surface soils is present in an inorganic, oxidized state as As(V) (Bissen and Frimmel 2003). In order to test the potential for study soils to be present in a more reduced state (As[III]), a Typic Hydrudands soil (10 cm depth) was collected during January (the rainy season) from a low-lying area under a heavy forest canopy. To avoid modification of *in situ* redox state, sampling was conducted under nitrogen atmosphere. Moisture content in the soil was approximately 60% of oven dry (105°C) soil mass. XANES spectra of the soil were obtained at SSRL and compared to standard spectra (Meharg et al. 2008) for arsenic species determination. Arsenic in this soil was determined to be inorganic and oxidized (As[V]). Reducing conditions in surface soils of Typic and Lithic Hydrudands are not expected to develop, due to the well-drained nature of the soil, especially for soils developed over porous aa lava. However, during periods of high water saturation, reducing conditions could potentially develop within the soil profile. Water saturation and reducing conditions are more likely to occur in soils overlying less permeable pahoehoe lava, or in Acrudoxic Hydrudands soils that have higher clay content and are poorly drained. Reduction of As(V) to As(III), in the slightly acidic study soils (5.5–6.5) in the presence of poorly crystalline iron oxyhydroxides (ferrihydrite, geothite), is not expected to result in increased arsenic mobility (Dixit and Hering 2003). However, reducing conditions could lead to dissolution of iron oxyhydroxide substrate (Pedersen et al. 2006), which could potentially lead to increased concentrations of dissolved arsenic in the soil solution and downward migration of arsenic within the soil column.

Arsenic Distribution in Surface Soils

Surface soil samples (N = 134 sample locations) were collected across the study area from Hilo to Pahoa, within and adjacent to known sugar cane cultivation areas. Naturally occurring background levels of As_{TOT} in soils not used for sugar cane cultivation are below 20 mg kg^{-1} (NCSS, 2011). Within former sugar cane cultivation areas (N = 100 sample locations), where arsenical herbicides were applied, soil As_{TOT} concentrations range from 39 to 880 mg kg^{-1}, with an average of 280 ± 190 mg kg^{-1} (mean ± 1 SD).

Soil As_{TOT} concentrations are similar among the major cultivation areas. Soil from within the limits of the former Waiakea Mill Company plantation (N = 53), and the Olaa/Puna Sugar Plantation (N = 47), exhibit similar mean As_{TOT} concentrations of 270 ± 220 and 290 ± 160 mg kg^{-1}, respectively. The mean As_{TOT} content in the Waiakea and Olaa/Puna plantation soils is not statistically different at the 95% confidence level (two-tailed t-test, $p>0.05$).

Detailed cultivation boundaries during the period of arsenical herbicide use (1913 to circa 1950) are available for the Waiakea and Olaa/Puna plantations from historical maps (Cook 1926, Williams 1933). Comparison of soil arsenic concentrations with cultivation boundaries clearly shows the relationship between sugar cane cultivation (and arsenical herbicide application) and elevated soil arsenic content (Figure 2). Throughout the study area, all known sugar cane cultivated areas have elevated soil arsenic levels. Some locations near Hilo Harbor that were not used for sugar cane cultivation, also show elevated soil arsenic, possibly due to application of arsenical herbicides for weed control around facilities and roadways. Historical sugar cultivation was present northwest of Hilo along the Hamakua Coast (Figure 1). No comprehensive mapping of soil arsenic is known for these areas, however preliminary work by the authors indicates that total arsenic levels in surface soils may be lower than observed for the Waiakea and Olaa/Puna plantations.

Vertical Extent of Arsenic in Hydrudands

Soil profiles were evaluated in two test pits, one each in Typic Hydrudands (Olaa Series) and Acrudoxic Hydrudands (Ohia Series), to evaluate the vertical distribution of arsenic contamination in former sugar cane lands. Fine fraction (<250 μm) samples from discrete depth intervals were analyzed for pH, TOC, total element composition (As, Fe, and P), reactive iron (and P) and As_{IVBA} (Appendix Table C.3).

The Typic Hydrudands (Olaa Series) profile (Figure 5) consists of 80 cm of soil development above aa lava (“clinker zone”) comprised of weathered basalt cobbles with significant interstitial porosity. Soils are dark brown in color, organic-rich, cobbly silty clay loams derived from weathering of both lava lithics and subsequent ash deposits. The Acrudoxic Hydrudands (Ohia Series) profile (Figure 6) shows a minimum of 90 cm of soil development (the underlying bedrock was not encountered). Parent material for the upper portions of the profile (Ap and Bw_1 horizons) is dominantly ash, with coarse weathered tephra lithics in dense ash substrate observed below 65 cm depth. Both profiles exhibit a narrow range of soil pH (5.7 to 6.2 ± 0.1). Total organic carbon content (TOC) ranges from 23 to 86 ± 0.5 g kg^{-1} in the more weathered Ohia soils and 94 to 123 ± 0.5 g kg^{-1} in the Olaa soil; in each profile, TOC is highest in the uppermost Ap horizon (plow zone).

Total arsenic in the Olaa soil profile ranges from 180 to 660 mg kg^{-1}, with concentrations dropping to 95 mg kg^{-1} at the contact between the soil profile and underlying weathered rock (80 cm depth) and to <10 mg kg^{-1} at 120 cm within weathered rock. Concentrations of As_{TOT} along the depth profile are highly variable, with peaks at 30 and 60 cm depths, separated by lower concentrations at 40 and 50 cm depths. In the Ohia profile, As_{TOT} is much lower than in the Olaa profile, ranging from <10 to 110 mg kg^{-1}. Similar to the Olaa profile, As_{TOT} is highly variable with depth, with peaks at 10 and 30 cm. Arsenic concentrations above "background" levels of 20 mg kg^{-1} are confined to the upper 50 cm of the Ohia soil profile.

The total phosphorus in the soil profiles ranges from approximately 1,000 to 3,000 mg kg^{-1}. Kau Basalt contains approximately 1,000 mg P kg^{-1} (Wolfe and Morris 1996), whereas naturally occurring background levels of P_{TOT} in surface soils of the study area (never under cultivation) are 1,000 to 1,500 mg P kg^{-1} (NCSS 2011). Use of phosphate-based fertilizers was common in Hawaiian sugar cane cultivation (Smith 1955), and included the application of bonemeal, monocalcium phosphate (superphosphate and triple superphosphate) and monoammonium phosphate (J. Cross, personal communication). Total phosphorus in soil above 1,500 mg kg^{-1} is probably the result of phosphorus-based fertilizer addition. Citrate-dithionite-extractable phosphorus (P_{CD}) in soil profiles ranges from 300 to 1,300 mg kg^{-1}. P_{CD} is believed to represent phosphorus in association with reactive iron substrate, which could include residual fertilizer compounds and a small fraction of igneous apatite (Ruttenberg 1992). Reactive phosphorus in soil is expected to behave similarly to inorganic arsenic in soil partitioning and mobility.

Total iron and aluminum are higher in the Acrudoxic Hydrudands (Ohia) profile than in the Typic Hydrudands (Olaa) profile. This is due to the relative enrichment in the ash-dominant profile as compared to a lithic-rich profile. Reactive iron pools are distinctly different in the two profiles. Fe_{HAH} content, indicative of highly reactive, poorly crystalline, ferrihydrite-like substrate, is relatively low in both profiles (approximately 10% of Fe_{TOT}). Fe_{CD}, indicative of both ferrihydrite-like compounds and more crystalline pedogenic iron oxyhydroxides or oxides forms, accounts for 40% of Fe_{TOT} in the Typic Hydrudands soil profile and nearly 80% of Fe_{TOT} in the Acrudoxic Hydrudands profile. The portion of Fe_{TOT} not dissolved by the citrate-dithionite reagent probably consists of primary iron silicate mineral phases or unweathered volcanic glass. The higher proportion of Fe_{CD} in Acrudoxic Hydrudands attests to the advanced weathered nature of the soil profile, and relative absence of partially weathered lithics.

Arsenic and phosphorus (phosphate in soil, $H_2PO_4^-$ and HPO_4^{2-}) appear to behave similarly in the two soil profiles. Phosphorus concentrations above background levels (1,500 mg kg^{-1}) are believed to reflect the application of phosphate fertilizers to sugar cane soils. Phosphate fertilizers were applied to the soil and potentially mixed by tillage to a depth of 20 to 25 cm (based on the use of disc harrows in Hawaii plantations; J. Cross, personal communication). Arsenical herbicides were sprayed on emergent weeds, and arsenic (overspray to soils and residual on dead weeds) was mixed into shallow soils by tillage. Test pit samples indicate the depth of penetration into the soil profile and location of concentration peaks are similar for arsenic and phosphorus. In the Olaa profile, coincident arsenic and phosphorus (P_{TOT} and P_{CD}) peaks are observed at 20–30 and 60 cm depths, and both arsenic and phosphorus concentrations approach background levels at a depth of 80 cm (the contact with underlying weathered rock). In the Ohia profile, As_{TOT} and phosphorus (P_{TOT} and P_{CD}) show coincident peaks at 10 and 30 cm depths, and both arsenic and phosphorus reach background levels between 40 and 50 cm depth. In both profiles, arsenic and phosphorus peaks are in part coincident with relative peaks in reactive iron (Fe_{HAH} and Fe_{CD}); increased arsenic and phosphorus retention within these specific horizons may be indicative of relatively higher iron oxyhydroxide content (a strong As and P sorbent) and lower lithic content (a weak As and P sorbent).

Downward migration of arsenic (and P) through the Hydrudands soil profiles may be mediated by several processes, including migration of dissolved arsenic in the soil solution (potentially accentuated by P-based fertilizer application), migration of soil colloids with sorbed arsenic, physical mixing by human cultivation (tilling), and bioturbation by plant roots and biota. Batch desorption studies were conducted on study soils (Hue and Cutler 2007) to evaluate the degree of arsenic solubility in DI water and a synthetic soil solution (0.01M $CaCl_2$). Results indicated very limited solubility, with no arsenic detected in solute at a method detection limit of approximately 1 μg L^{-1}. Sequential extraction with $CaCl_2$ and Mehlich III reagents showed arsenic desorption at low concentrations (Hue 2012, Hue and Cutler 2007), which indicated arsenic may be mobile to some degree in the soil solution over time. During periods of high water saturation, reducing conditions may develop in the soil column, and dissolution of iron oxyhydroxide phases may occur resulting in increased release of sorbed arsenic to the soil solution. The degree to which redox fluctuations affect arsenic mobility in study soils is not known; to date no *in situ* measurements of soil redox potential or collection/analysis of soil solutions have been undertaken. Arsenic desorption to the soil solution and transport downward transport may have been accentuated by competitive desorption by dissolved phosphorus, which would have increased in the soil solution after P-based fertilizer application (every two years prior to cane planting). The migration of soil colloids has been shown to facilitate heavy metal migration in soil columns. Karathanasis (1999) showed that water-dispersible soil colloids can accentuate the mobility of Cu and Zn in some soils, however the study showed that lower metal transport potential occurred in colloids with high iron and aluminum hydroxide content (as is likely in Hydrudands of this study).

Bioturbation may be in part responsible for physical mixing of soils and downward flux of soils during macropore formation and collapse (Gabet et al. 2003). Plant roots and associated macropores were observed in the Ohia profile extending through the entire 80 cm soil column and into underlying aa lava. At present, this location is vegetated with guinea grass and coconut palms. In the Ohia profile, where agricultural practices have continued even though sugar cane cultivation ceased, evidence of intensive plant root bioturbation extends to a depth of about 55 cm. In both profiles, evidence of intense plant root bioturbation is present throughout the zone of elevated arsenic contamination, and may be a factor in the downward transport of soil arsenic and the development of vertical distribution of arsenic in the soil profiles.

For the soil profiles inspected in the study area, arsenic migration did not extend below materials with strong arsenic sorption capacity (Figures 5 and 6); therefore, the underlying groundwater resources does not appear to be at risk from arsenic contained in overlying soils. This does not preclude the potential for arsenic to affect groundwater in other site scenarios, especially where soils are thin, the groundwater is shallow, and a significant arsenic source in soil is present (e.g., an arsenic release at a chemical storage or mixing facility).

Bioaccessible Arsenic in Surface Soils and Vertical Profiles

Bioaccessible arsenic was evaluated in surface soils (N = 26 sample locations) using the SBRC-g test method. As_{IVBA} (concentration basis) ranges from 1.6 to 76 mg kg^{-1} (Figure 7), whereas As_{IVBA} (percentage basis) ranges from 1.6 to 35% (Table 2). Most soils evaluated were Typic or Lithic Hydrudands (N = 19), with a smaller number of Acrudoxic Hydrudands (N = 6) and only one Udifolists. As previously mentioned, the Udifolists soils are generally not developed enough to support sugar cane cultivation, only one location with Udifolists soil was identified that may have been in sugar cane cultivation. Acrudoxic Hydrudands, with higher total iron and reactive iron (Fe_{CD}) content, and a lower percentage of lithics and organics, show the lowest percent bioaccessibility, averaging 4.1 ± 2% for the 6 soils tested (Table 3). Typic and Lithic Hydrudands, which display a range of soil properties between highly weathered Acrudoxic Hydrudands and incipient Udifolists, average 9.2 ± 5% As_{IVBA}. The single Udifolists evaluated for As_{IVBA} showed 35% bioaccessibility, by far the highest percent As_{IVBA} value observed in former sugar cane surface soil of the study area. A cross-plot of As_{TOT} versus As_{IVBA} (Figure 7) displays the high variability in the percentage of arsenic bioaccessibility in surface soils of the study area. However, the trend of decreasing arsenic bioaccessibility with increasing soil weathering (Udifolists > Typic and Lithic Hydrudands > Acrudoxic Hydrudands) is apparent. Comparison of arsenic bioaccessibility with Fe_{CD} further supports the finding of lower bioaccessibility in more weathered Andisols (Figure 8). Study soils are limited to Andisols (and a few Histosols) from the Island of Hawaii, and it is not known at this time whether the degree of arsenic bioaccessibility continues to decrease as Andisols further weather to other soil orders (i.e., Oxisols or Ultisols).

Bioaccessible arsenic was determined for soils in the two vertical soil profiles (Appendix Table C.3). For the Typic Hydrudands profile, As_{IVBA} (percentage basis) is highest in the Ap horizon (surface soils at 10 and 20 cm depth) averaging about 8% of As_{TOT}. In the weathered subsoils (Bw horizon, 30 to 60 cm depth), As_{IVBA} averages approximately 4% of As_{TOT}; these Bw horizon soils contain a higher percentage of potential arsenic sorbents (reactive Fe and Al phases). The weathered rock zone below 80 cm depth has low concentrations of As_{TOT} (8 to 32 mg kg^{-1}), and low As_{IVBA} (percentage basis) that may be related to the low As_{TOT} loading (Cutler 2011). The Acrudoxic Hydrudands profile shows significantly lower As_{IVBA} than the less weathered Typic Hydrudands, averaging about 2% of As_{TOT} in the Ap and Bw horizons.

Bioaccessible Arsenic and the Need for Mitigating Actions

Soil arsenic concentrations above naturally occurring background levels are ubiquitous in former sugar cane lands in the eastern portion of the Island of Hawaii. The average As_{TOT} concentration in surface soils (N = 100) of the former Waiakea and Olaa/Puna sugar cane plantations is approximately 280 mg kg^{-1}, ranging from 39 to 880 mg kg^{-1} (SD = 190 mg kg^{-1}). Soils used for sugar cane cultivation are Hydrudands, a great group of the Andisol soil order. Hydrudands are characterized by hydrated, short-range order iron oxyhydroxides, aluminosilicates, and aluminum-iron-humus complexes, and have a strong propensity to adsorb oxyanions such as phosphate and inorganic arsenic (arsenite/arsenate). As a result of historical application of sodium arsenite herbicide solutions, high levels of residual arsenic are found in shallow soils. While the properties of Hydrudands leads to sequestration of arsenic, and arsenic soil contamination, the strong binding capacity of these soils also limits its release in the soil solution and in the *in vitro* bioaccessibility test. As such, the soil properties that led to high arsenic sequestration also prevents arsenic migration to the underlying groundwater aquifer and limits its bioaccessibility and potential for human health hazard from incidental soil ingestion.

The average arsenic bioaccessibility in the Typic and Lithic Hydrudands study area is approximately 9 ± 5% of As_{TOT}, and for the more weathered Acrudoxic Hydrudands is only 4 ± 2% of As_{TOT}. Bioaccessible arsenic, expressed in concentration form, ranged from 1.6 to 76 mg kg^{-1} in a subset of soils evaluated by the SBRC-g *in vitro* test. More weathered soils, formed predominantly from volcanic ash, such as the Acrudoxic Hydrudands, showed a lower percentage of As_{IVBA} than Hydrudands (at similar As_{TOT} loadings) with a substantial lithic content. Incipient organic soils, the Udifolists, show a higher percentage of As_{IVBA}, although they were rarely used for sugar cane cultivation due to their poor development and shallow nature.

One Typic Hydrudands from the study area was tested for both *in vivo* relative arsenic bioavailability in the cynomolgus monkey model (Roberts et al. 2007) and *in vitro* bioaccessibility by the SBRC method (Exponent 2005, Lowney et al. 2007). Measured relative arsenic bioavailability (5 ± 2%) and bioaccessibility (6.5%, no uncertainty provided) were similar, suggesting the SBRC-g test may be a valid surrogate for the costly *in vivo* test. Work on Australian soils (Juhasz et al. 2007, 2009) indicated a strong correlation between *in vivo* relative arsenic bioavailability in juvenile swine and $\mathrm{As}_{\mathrm{IVBA}}$ (SBRC-g method). Recent work comparing mouse *in vivo* bioavailability with SBRC-g $\mathrm{As}_{\mathrm{IVBA}}$ also exhibited a strong correlation (Bradham et al. 2011). To evaluate the appropriateness of *in vitro* methods and to better gauge the potential for human health risks from soil arsenic exposure, the authors recommend additional *in vivo* bioavailability work on arsenic-contaminated Hawaiian soils.

Hawaii Department of Health (2006, 2010) published recent guidance on the management of arsenic-contaminated soil, using $\mathrm{As}_{\mathrm{IVBA}}$ to assess potential human health direct-contact hazard and the need for remedial actions. An average $\mathrm{As}_{\mathrm{IVBA}}$ concentration of 23 mg kg^{-1} was identified by HDOH (2010) as an action level, corresponding to a non-cancer hazard quotient of 1.0 and an excess lifetime cancer risk of $5\mathrm{E}^{-5}$ under a residential exposure scenario (HDOH 2006). Land with soils containing $\mathrm{As}_{\mathrm{IVBA}} \leq 23$ mg kg^{-1} (on average) are deemed “minimally impacted,” and do not require specific land use controls or remedial action. Soils with $\mathrm{As}_{\mathrm{IVBA}} > 23$ mg kg^{-1} typically require remediation, engineering controls or restricted land use (e.g., no residential housing, schools, or day care centers). Based on the findings of this study, many land parcels within former sugar cane plantation fields are likely to have soils with $\mathrm{As}_{\mathrm{IVBA}}$ levels ≤ 23 mg kg^{-1}, and will not require mitigating actions pursuant to HDOH guidance. Higher levels of arsenic soil contamination have been identified by HDOH in areas where arsenic-based herbicides were previously stored or mixed, with concentrations of bioaccessible arsenic commonly above 100 mg kg^{-1} and in some cases exceeding 1,000 mg kg^{-1}. Bioaccessible arsenic testing allows rapid identification of lands within former sugar cane operations where residual soil arsenic could pose significant risk to human health, triggering the need for some form of remedial action or land use controls.

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Figures

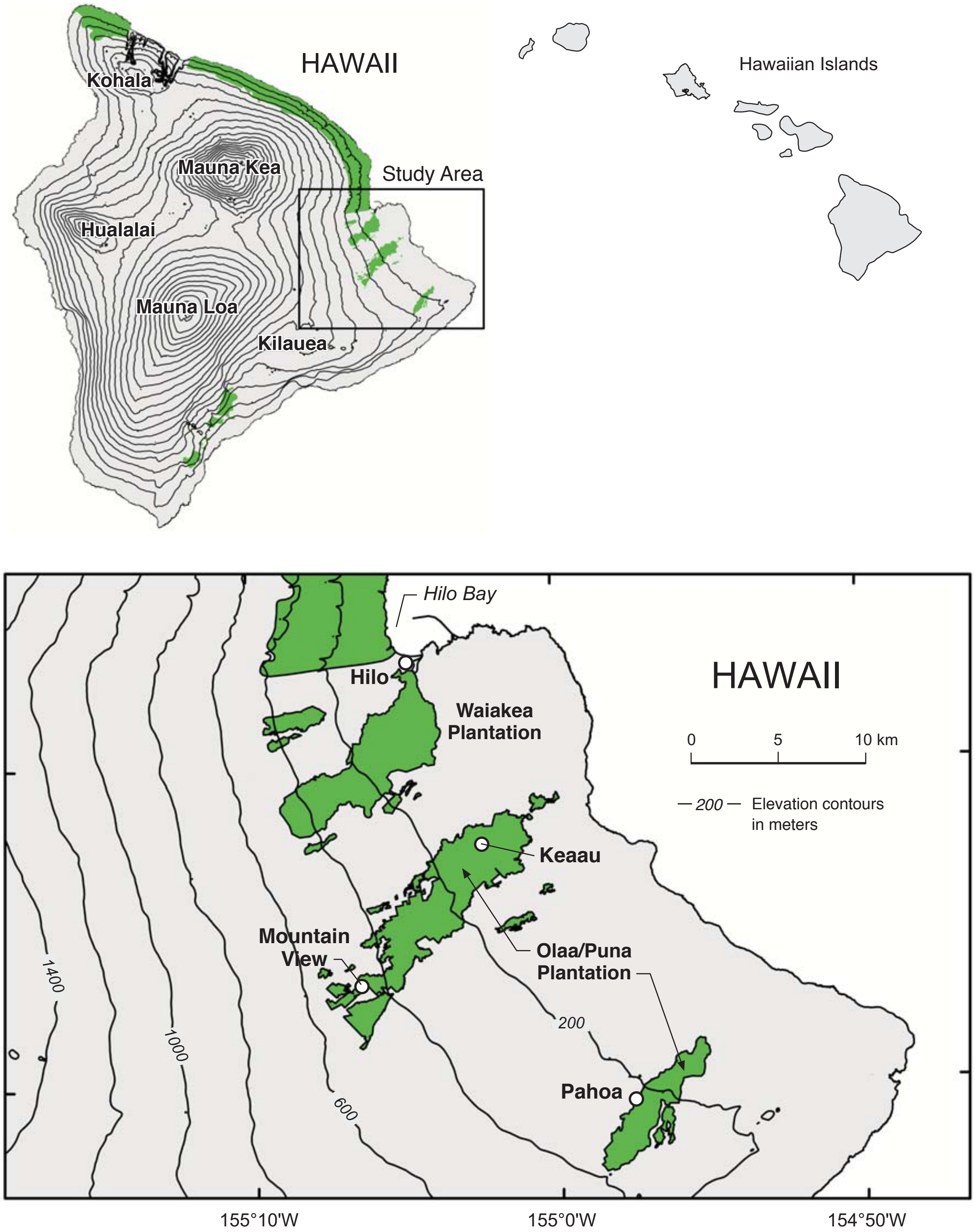


Figure 1. Extent of sugar cane cultivation on the Island of Hawaii during the 1920s and 1930s, when arsenic was the primary herbicide. Plantation boundaries derived from Cook (1926), Williams (1933) and Territory of Hawaii (1939). Study area includes several discontinuous sugar cane plantations south of the town of Hilo on the eastern flanks of the Mauna Loa and Kilauea volcanoes.

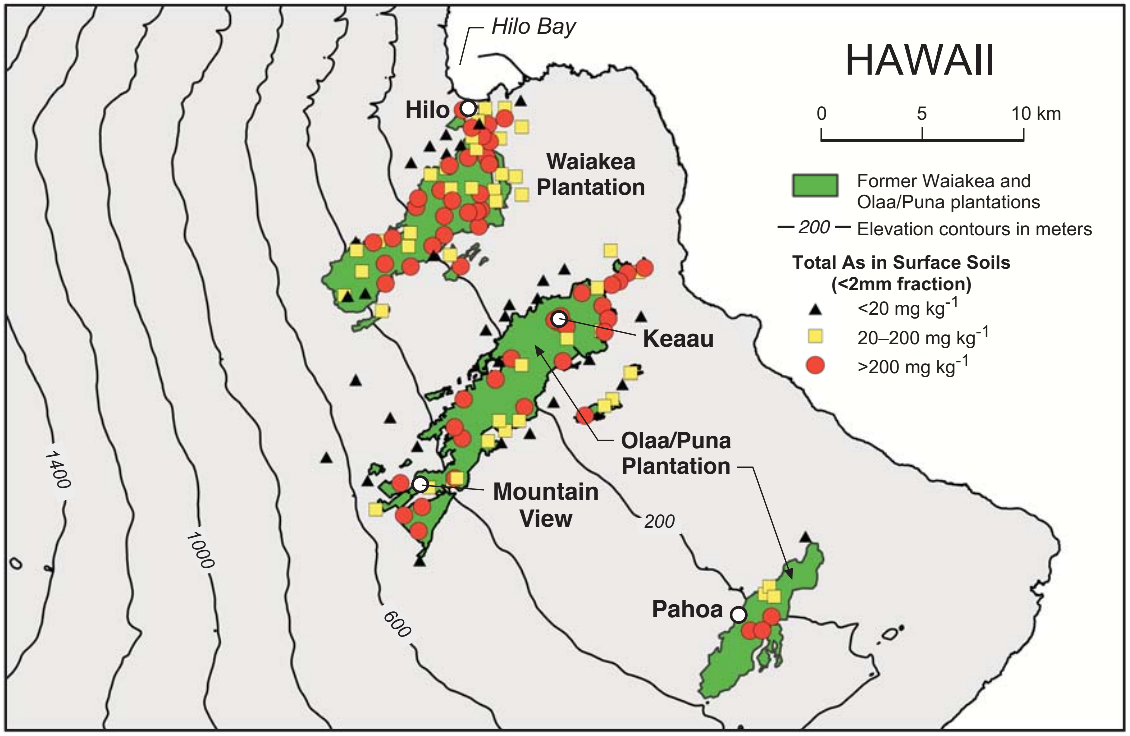


Figure 2. Total arsenic concentrations in surface soils of former sugar cane plantations average 280 mg kg^{-1}, and are at natural background concentrations (<20 mg kg^{-1}) outside of sugar cane cultivation areas.

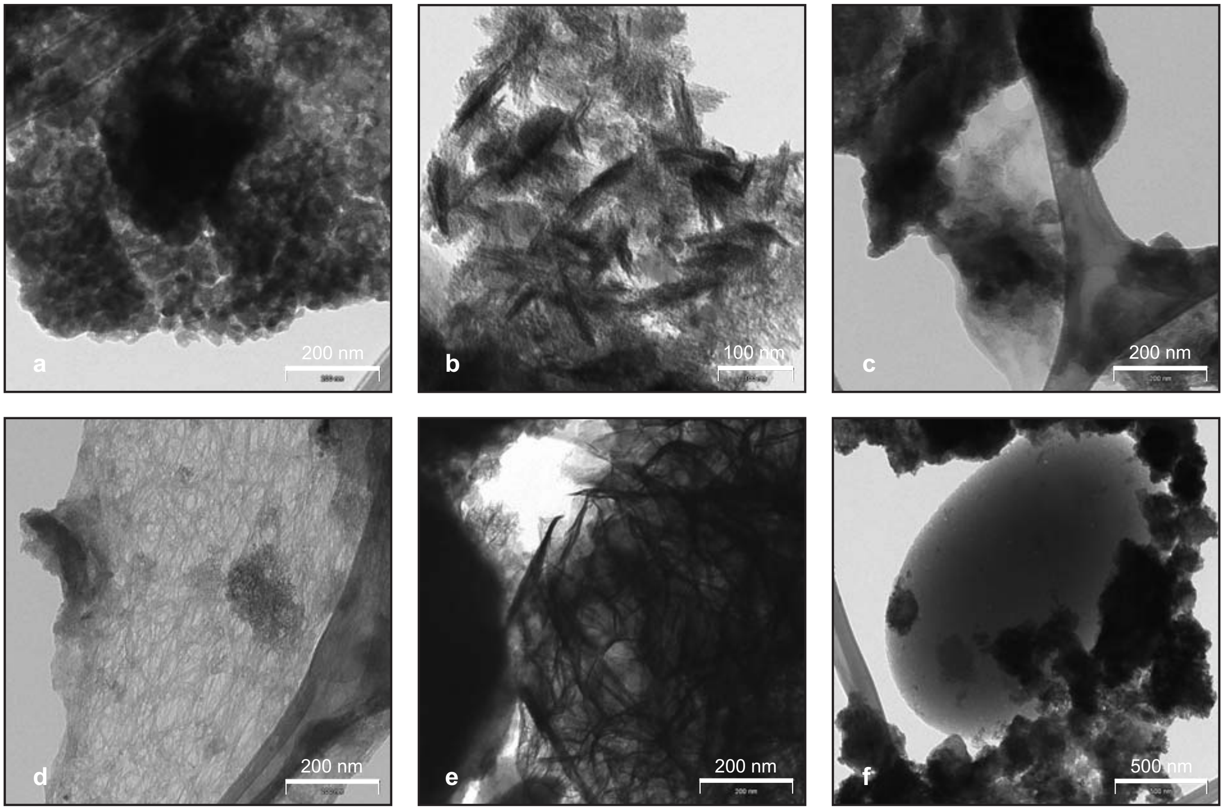
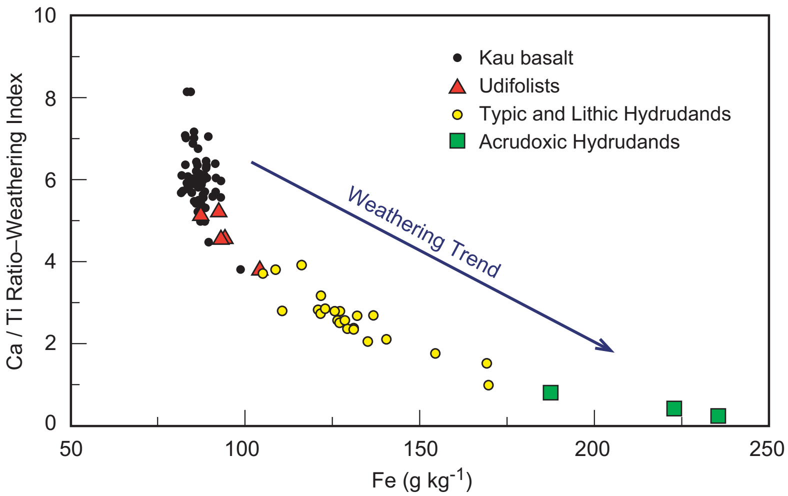
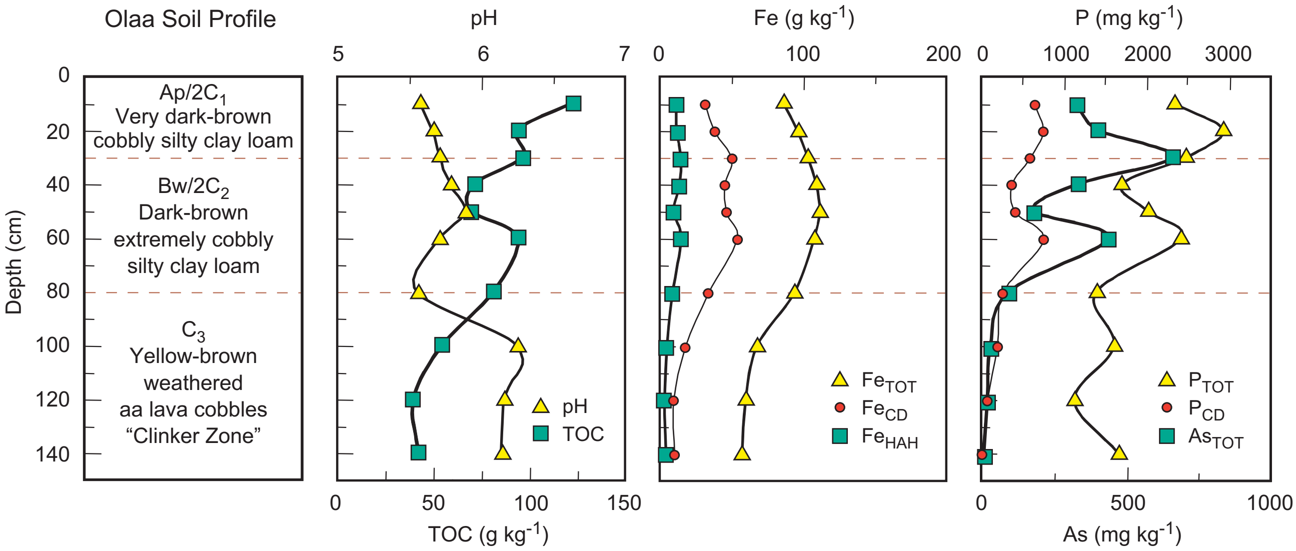


Figure 3. TEM photomicrographs of soil solid phase materials: (a) ferrihydrite-like Fe oxyhydroxide, (b) incipient goethite in ferrihydrite, (c) gel-like material clinging to sample frame, (d) imogolite (aluminosilicate), (e) smectite, and (f) opaline silica surrounded by Fe oxyhydroxide aggregates.



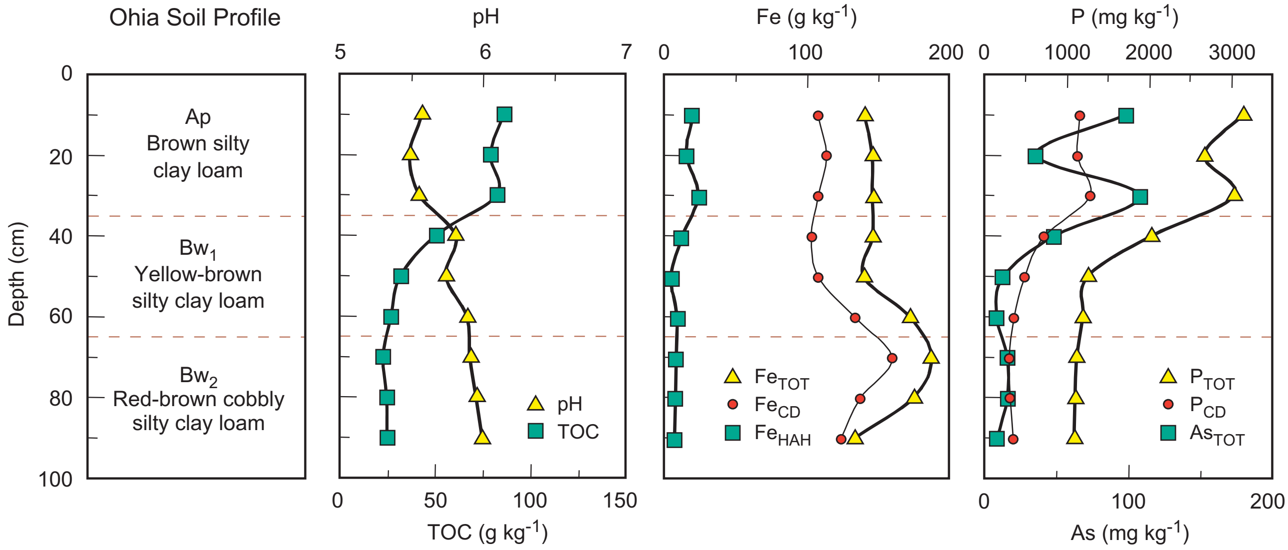
Note: Coefficient of variation for replicate Fe analyses is 0.5% and 6% for Ca/Ti ratio.

Figure 4. Ca/Ti elemental ratio and Fe content are useful indicators of the degree of volcanic soil weathering in the study area, Island of Hawaii. Iron content increases and Ca/Ti ratio decreases as soils weather from parent material compostion (Kau Basalt), ultimately leading to most weathered soil type (Acrudoxic Hydrudands).



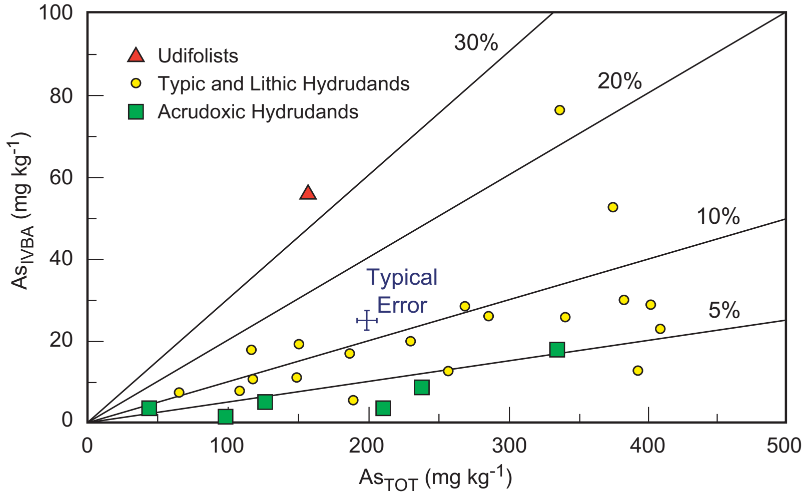
Note: Data are provided in Appendix Table C.3.

Figure 5. Vertical soil profile of a Typic Hydrudands (Olaa Series), Island of Hawaii.



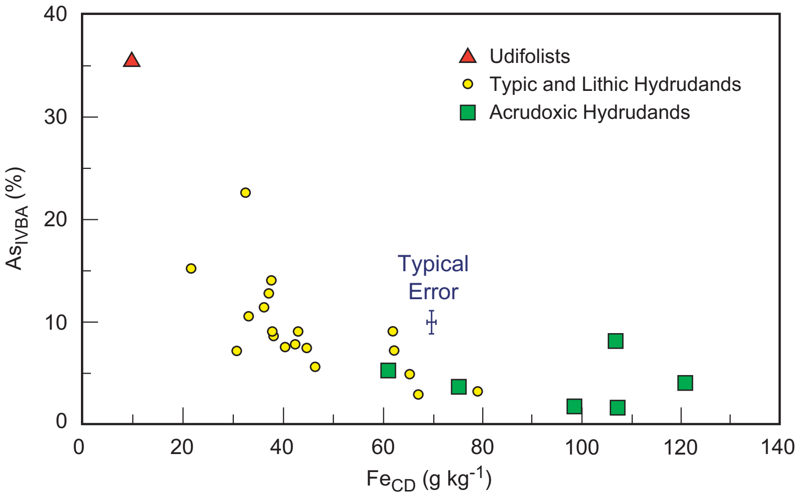
Note: Data are provided in Appendix Table C.3.

Figure 6. Vertical soil profile of an Acrudoxic Hydrudands (Olaa Series), Island of Hawaii.



Note: Coefficient of variation is 6% for As_{TOT} and 9% for As_{IVBA}, as shown by "typical error" bars.

Figure 7. Comparison of bioaccessible arsenic (As_{IVBA}; concentration form) with total arsenic (As_{TOT}) in surface soils of study area, with lines of constant percentage As_{IVBA} shown. The most weathered Andisols, Acrudoxic Hydrudands, have low As_{IVBA} relative to other soils.



Note: Typical error bars are based on coefficient of variation of 1.2% for Fe_{CD} and 11% for As_{IVBA}.

Figure 8. Comparison of bioaccessible arsenic (As_{IVBA}; percentage basis) with reactive iron (Fe_{CD}) in surface soils shows inverse relationship between As_{IVBA} and Fe_{CD}, with lower bioaccessibility in more weathered Andisols.

Tables

Table 1. Major element composition of Kau Basalt and associated surface soils, Island of Hawaii.

Matrix	Name	Age Underlying Lava[b] (years)	Concentration in mineral solids[a] (g kg^{-1})										
			N[c]	Si	Ti	Al	Fe	Mn	Mg	Ca	Na	K	P
Rock	Kau Basalt[d]		63	234 ± 7	11 ± 2	66 ± 10	87 ± 3	1.3 ± 0.1	70 ± 30	67 ± 9	15 ± 3	2.7 ± 1.0	1.0 ± 0.2
Soil	Udifolists	<3,000	5	235 ± 6	15 ± 1.1	75 ± 7	94 ± 6	1.5 ± 0.1	47 ± 6	70 ± 6	9.5 ± 1.9	3.8 ± 0.3	2.8 ± 1.1
Soil	Typic and Lithic Hydrudands	3,000–10,000	23	193 ± 15	16 ± 3	87 ± 15	130 ± 16	1.8 ± 0.2	90 ± 20	40 ± 8	3.5 ± 1.6	2.0 ± 0.5	3.6 ± 1.7
Soil	Acrudoxic Hydrudands	10,000–30,000	4	110 ± 18	35 ± 4	170 ± 14	220 ± 20	2.8 ± 0.1	23 ± 9	14 ± 7	0.8 ± 1.3	2.2 ± 0.2	6.3 ± 1.8

[a] Element concentrations for soils (0–20 cm depth; <2 mm fraction) by WDXRF reported (mean ± 1 SD) in dry weight basis after furnace combustion at 750°C.
[b] Lava ages based on data from Wolfe and Morris (1996).
[c] Number of rock or soil samples analyzed.
[d] Kau Basalt chemistry by WDXRF from Wolfe and Morris (1996).

Table 2. Total and bioaccessible arsenic in surface soils, eastern portion of Island of Hawaii.[a]

ID	Soil Type[b]	As_{TOT}[c] (mg kg^{-1})	As_{IVBA}[d] (mg kg^{-1})	As_{IVBA}[e] (%)	Fe_{TOT}[f] (g kg^{-1})	Fe_{CD}[g] (g kg^{-1})
HLO-08	Acrudoxic Hydrudands	210	3.7	1.8	132	99
KIP-10	Acrudoxic Hydrudands	99	1.6	1.6	139	107
SHP-14	Acrudoxic Hydrudands	130	5.2	4.0	145	121
SHP-49	Acrudoxic Hydrudands	340	18	5.2	112	61
SHP-51	Acrudoxic Hydrudands	240	8.8	3.7	121	76
SHP-53	Acrudoxic Hydrudands	44	3.6	8.1	147	107
HLO-05	Lithic Hydrudands	150	11	7.4	96	45
HLO-11	Lithic Hydrudands	390	13	3.3	143	79
HLO-12	Lithic Hydrudands	190	5.6	2.9	118	67
SHP-23	Lithic Hydrudands	120	18	15	81	22
SHP-26	Lithic Hydrudands	340	26	7.6	100	41
SHP-40	Lithic Hydrudands	65	7.4	11	99	36
HLO-02	Typic Hydrudands	110	7.8	7.1	110	62
KMS-5	Typic Hydrudands	380	30	7.9	99	43
SHP-03	Typic Hydrudands	340	76	22	88	33
SHP-07	Typic Hydrudands	290	26	9.0	70	38
SHP-08	Typic Hydrudands	380	53	14	93	38
SHP-10	Typic Hydrudands	150	19	13	68	37
SHP-17A	Typic Hydrudands	190	17	8.9	98	43
SHP-24	Typic Hydrudands	270	28	11	94	33
SHP-27	Typic Hydrudands	120	11	8.9	97	62
SHP-30	Typic Hydrudands	260	13	4.9	123	66
SHP-34	Typic Hydrudands	230	20	8.6	95	38
SHP-43	Typic Hydrudands	410	23	5.6	100	47
STS-010	Typic Hydrudands	400	29	7.2	89	31
SHP-36	Typic Udifolists	160	56	35	62	9.9
N		26	26	26	26	26
Minimum		44	1.6	1.6	62	9.9
Maximum		410	76	35	147	121
Average		231	20	9.0	104	55
SD		114	18	7	23	28

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[a] 0–20 cm depth; < 0.25 mm soil fraction.

[b] From Soil Survey Staff (2010).

[c] Replicate As_{TOT} measurements (N = 4) of NIST 2710 control soil indicate error (CV) of 6%.

[d] Replicate measurements of As_{IVBA} (concentration basis) have error (CV) of 9%.

[e] Replicate measurements of As_{IVBA} (percentage basis) display CV of 11%.

[f] Replicate measurements of Fe_{TOT} display CV of 1.3%.

[g] Replicate measurements of Fe_{CD} display CV of 1.2%.

Table 3. Bioaccessible arsenic and reactive iron in surface soils of former sugar plantations, eastern portion of Island of Hawaii.[a]

Soil Type	N	As_{IVBA} (%)[b]			Fe_{CD} (g kg^{-1})[c]		
		Min	Max	Mean ± SD	Min	Max	Mean ± SD
All Soils	26	1.6	35	9.0 ± 7	10	121	55 ± 28
Acrudoxic Hydrudands	6	1.6	8.1	4.1 ± 2	61	121	95 ± 22
Typic and Lithic Hydrudands	19	2.9	22	9.2 ± 5	22	79	45 ± 15
Udifolists	1			35			9.9

[a] 0–20 cm depth; < 250 μm soil fraction.
[b] Replicate measurements of bioaccessible arsenic (As_{IVBA}, percentage basis) display coefficient of variance (CV) of 11%.
[c] Replicate measurements of citrate-dithionite extractable iron (Fe_{CD}) display CV of 1.2%.

Appendices

Appendix A

Supplemental Information

Supplemental Information

History of Arsenical Herbicide Use in Study Area

Sugar cane cultivation was introduced to Hawaii by Polynesian voyagers and settlers a millennium before the arrival of westerners. Cultivation expanded significantly beginning in the mid-1800s and quickly became the backbone of the Hawaii economy. Plantations were widespread in the eastern portion of the Island of Hawaii on the lower windward slopes of the Mauna Kea, Mauna Loa and Kilauea volcanoes from the mid-1800s until the late 1900s, when the majority of the sugar cane cultivation in Hawaii came to an end due to competition from abroad (Dorrance and Morgan 2000). Plantations were established where soil development was sufficient, below elevations of 600 m above mean seal level. These locations exhibit a mean annual temperature of 20.5°C, and an annual rainfall of approximately 4,000 mm (Giambelluca et al. 2011). North of Hilo Bay, along the Hamakua Coast on the northeast flank of Mauna Kea, sugar cane was cultivated in nearly contiguous tracts of land (Figure 1). South of Hilo Bay, sugar cane was cultivated in discontiguous parcels defined by older lava flows with adequate soil development. The current study area includes lands within South Hilo and Puna districts of the Island of Hawaii, and extends southeast from Hilo Bay to the town of Pahoa, and southwest to Mountain View. Two large plantation complexes were established within the study area: the Waiakea Mill Company plantation near Hilo (1879 to 1947) and the Olaa Sugar Company (later called Puna Sugar Company) plantation (1900 to 1982). The Waiakea Mill Company plantation extended from the town of Hilo 10 km up the flanks of Mauna Loa to the southwest, to an elevation of approximately 500 m above sea level. The Olaa/Puna plantation consists of contiguous plantation lands extending from the towns of Keaau to Mountain View, with isolated plantings further south in the vicinity of the town of Pahoa (Figure 1). Sugar cane cultivation reached its full historic extent by the 1920s (Territorial Planning Board 1939, Dorrance and Morgan 2000), extending across approximately 60 km^2 (6,000 hectares) within the study area. Sugar cane cultivation in the Waiakea plantation ceased in 1947, and the town of Hilo expanded across the former sugar cane lands. At higher elevations above Hilo, and across much of the former Olaa/Puna plantation, current land use consists of diversified agriculture (papaya, macadamia nuts, and ornamentals), low-density residential development and fallow land.

Arsenical herbicides were first used in the State of Hawaii in 1913 at the Olaa plantation (Larsen 1914a), and eventually expanded to other plantations throughout Hawaii (Larsen 1914b). A concentrated sodium arsenite stock solution was prepared by dissolving arsenic trioxide (white arsenic) in aqueous sodium hydroxide; then further diluting the stock solution with water for application in the fields by farm workers using sled or knapsack sprayers (Larsen 1914a, Hance 1938) (Supplemental Figure S1). By the late 1940s, the widespread use of arsenical herbicides ceased, and was replaced by synthetic organic herbicide compounds (pentachlorophenol [PCP] and 2,4-dichlorophenoxyacetic acid [2,4-D]) (Hance 1948, Hanson 1959).

Soil Mineralogy and Major Element Content

The fine silt and clay fraction (<10 μm) of Ap and Bw horizons of Typic Hydrudands were examined by TEM to identify dominant secondary solid phases based on surface morphology, internal microstructure and electron transmissivity (Figure 3). The dominant solid-phase materials observed were finely crystalline iron oxyhydroxides (ferrihydrite-like), aluminosilicates (allophane and imogolite), and non-crystalline gel materials. Less abundant phases included layer silicates (halloysite, smectite), opaline silica, and partially weathered volcanic glass. In general, short-range order materials—ferrihydrite, allophane-like materials and gels—dominated the humus-rich shallower Ap horizons. In the deeper Bw horizon soils with lower humus content, more crystalline mineral phases—ferrihydrite (minor goethite), imogolite and layer silicates (halloysite, smectite)—were observed along with significant quantities of short-range order phases. The increased crystallinity of the solid phases in the deeper/older soils is believed to be the result of less humus impeding the crystal arrangement and more time for the crystal growth (Schwertmann 1988).

These findings are consistent with those reported by other researchers of volcanic-ash soils. Soils derived from volcanic tephra display a unique assemblage of pedogenic solid phases, such as ferrihydrite, allophane, imogolite and opaline silica (Dahlgren et al. 1993). Reactive iron and aluminum compounds in gel or short-range order forms predominate, and their high reactivity (readily extracted by citrate-dithionite or ammonium oxalate reagents) is central to the definition of Andisols. In particular, reactive iron and aluminum compounds have high specific sorption capacity for oxyanions like phosphate and arsenite/arsenate. Organic content (humus) is abundant in young Andisols. Iron in soils is generally more stable in oxide forms than in humus complexes (Wada and Higashi 1976), and the dominant short-range order iron oxyhydroxide is ferrihydrite (Schwertmann and Taylor 1989). The presence of organics, silicate or phosphate in soil solutions tends to inhibit the crystal growth of ferrihydrite, and leads to short-range order structure (Schwertmann 1988). In organic-rich soils, humus preferentially complexes with aluminum, leaving little aluminum available to form aluminosilicates (Nanzyo et al. 1993). Humus complexed with aluminum or iron is not readily biodegraded, and tends to accumulate in Andisols. Allophane-like constituents are short-range order hydrous aluminosilicates with a range of compositions and morphologies. Aluminum-rich allophanes (Al:Si atomic ratio ~2:1) are the most commonly observed (Parfitt and Kimble 1989). Imogolite is a distinct aluminosilicate phase with composition similar to aluminum-rich allophanes with a thread-like structure indicative of longer range ordering (Parfitt and Henmi 1980). Gel-like materials are commonly observed in Andisols, forming coatings on soil mineral surfaces or binding soil aggregates (Jones and Uehara 1973, Jones and Fox 1978). Gel materials in Hawaiian Andisols are composed of oxides of aluminum, iron, and silicon and associated organic compounds (Hudnall 1977), and have been shown to be very reactive with respect to phosphate sorption (Jones and Fox 1978).

Major element composition of soils within the study area is variable, and related to the age, provenance, and weathering history of parent volcanic materials. The degree of soil weathering can be inferred from deviations of elemental compositions from parent rock compositions. Surface soils (N = 32) were evaluated for major element composition by wave dispersive (WD) XRF, and compared to whole rock compositions of the parent Kau Basalt provided by Wolfe and Morris (1996) and Sherrod et al. (2007). Weathering processes modify the bulk elemental composition of the soil. Certain elements tend to accumulate as soils weather, whereas others are depleted. Of the major elements sourced by the parent basalt rock, aluminum, titanium, manganese, and iron accumulate, while silicon, sodium, and calcium are depleted (Cutler 2011).

Previous studies recommended weathering indices for Hawaiian soils, using depleting (mobile) or accumulating (immobile) elements. Vitousek et al. (1997) used zirconium as an immobile index element in evaluating Hawaiian soil weathering; whereas Atkinson (1969) used sodium and calcium loss, and titanium gain, in developing regression equations for predicting the degree of weathering of young basalt lavas and incipient soils in the eastern portion of the Island of Hawaii. The ratio of a depleting to an accumulating element provide a useful indicator of the degree of volcanic soil weathering, and is more pronounced than changes observed for single elements. In Udifolists and Hydrudands of the study area, the Ca/Ti ratio decreases substantially with progressive soil weathering, and shows a strong inverse non-linear relationship with total iron content, which increases as soils weather (Figure 4). During parent rock and soil weathering, calcium, and other nonhydrolyzing cations (Na and Mg) are depleted by weathering, whereas iron, aluminum, and titanium accumulate by forming relatively immobile oxides and complexing with humus (Chorover et al. 2004). We found that the Ca/Ti ratio is a useful indicator of the degree of soil weathering in the study area soils, and can be evaluated in both the field and laboratory by energy dispersive (ED) XRF; these two elements have nearby Kα fluorescence peaks on EDXRF spectra (at 3.7 and 4.6 keV, respectively) allowing qualitative assessment of the degree of soil weathering from the basaltic parent material by visual inspection of the spectra.

The Ca/Ti ratio may not have broad application beyond young Histosols and Andisols, as calcium can be almost completely depleted in older soils. In addition, calcium may be magnified in shallow soils by plant re-deposition in litterfall or anthropogenically elevated by calcium-containing fertilizers, including bone meal (late 1880s and early 1900s), superphosphate [$Ca(H_2PO_4)_2$], or hydrated lime [$Ca(OH)_2$] (Smith 1955). In such cases, alternate element ratios, such as the Sr/Zr elemental ratio, may be a better indicator of the degree of soil weathering. Surface soil (0–20 cm) compositions, stratified by soil type, show an evolution of major element distributions (Table 1). Iron in the Kau Basalt, the dominant parent rock for the study area soils, averages 87 ± 3 g kg^{-1} (mean ± standard deviation [SD], N = 63). In incipient soils formed on basalt (Udifolists), iron is slightly enriched at about 94 ± 6 g kg^{-1} (mean ± SD, N = 5) (concentration in mineral solids after furnace combustion, which removes all water and organic compounds). In more weathered Typic and Lithic Hydrudands, iron averages almost twice the basalt content (130 ± 16 g kg^{-1} [mean ± SD, N = 23]), and is approximately three times the basalt concentration in Acrudoxic Hydrudands (220 ± 20 g kg^{-1} [mean ± SD, N = 4]), the most highly weathered soil in the study area. Soils were formed by weathering of basaltic parent material (i.e., lava and tephra), which led to progressive enrichment in titanium, aluminum, iron, manganese, and phosphate; and depletion of silicon, magnesium, calcium, and sodium. Although new tephra (principally ash) was introduced episodically to the top of the soil column after the last lava placement, surface soils show a degree of weathering consistent with the age of the underlying lava flows. Udifolists developed over the youngest lavas (<1,500 years old), and exhibit elemental compositions similar to the parent basalt. Soils developed over older lavas show progressive deviation from the original basalt composition. The more highly weathered state of surface soils above the older flows is partially due to the age of soil solids, but it is also a function of the relative contribution of faster-weathering ash versus slower-weathering basalt lithics. In Typic and Lithic Hydrudands, basalt lithics in varying states of weathering constitute more than 50% (and as much as 90%) of the soil mass, whereas basalt lithics generally constitute less than 5% of most Acrudoxic Hydrudands. The rapid weathering of ash and formation of pedogenic mineral phases, especially in warm, humid climates, has been well documented (Shoji et al. 1993).

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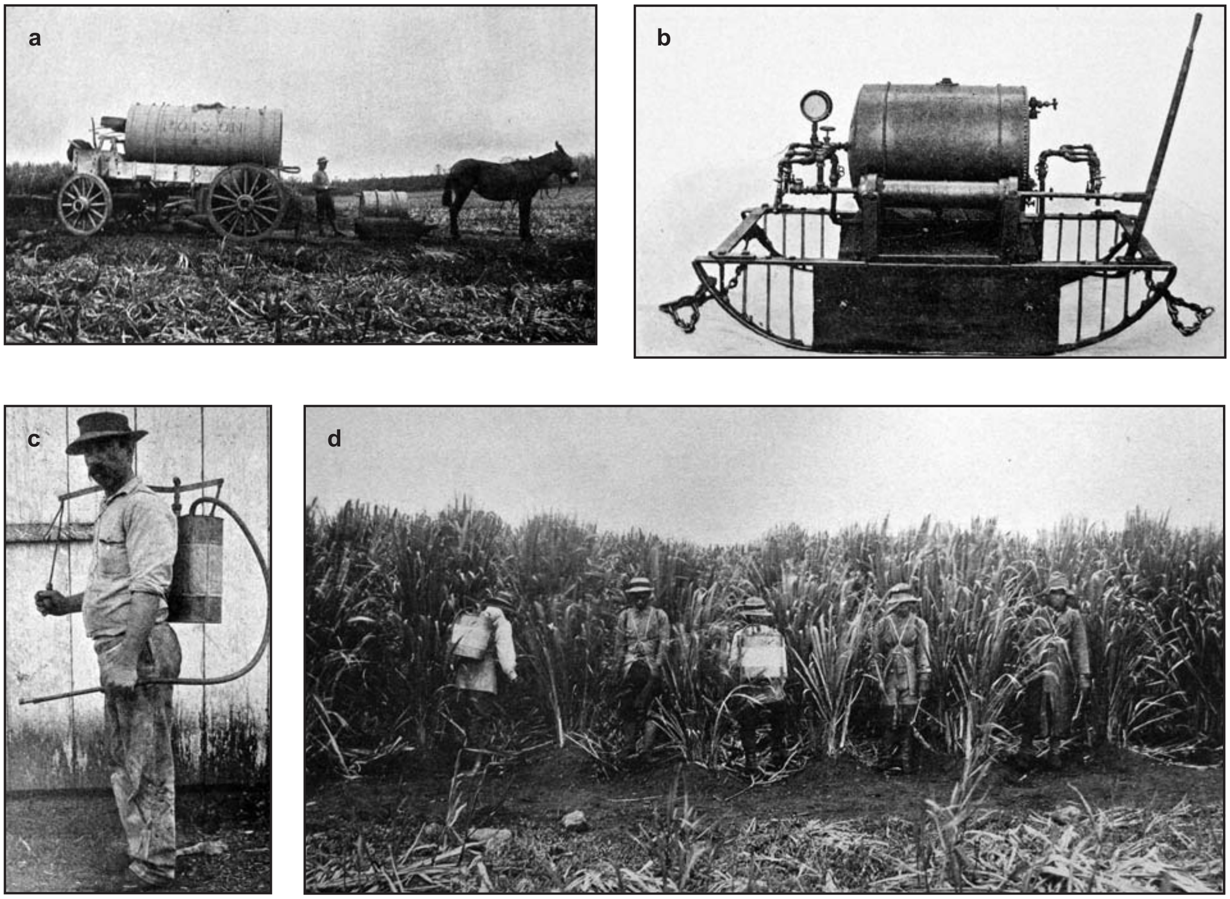
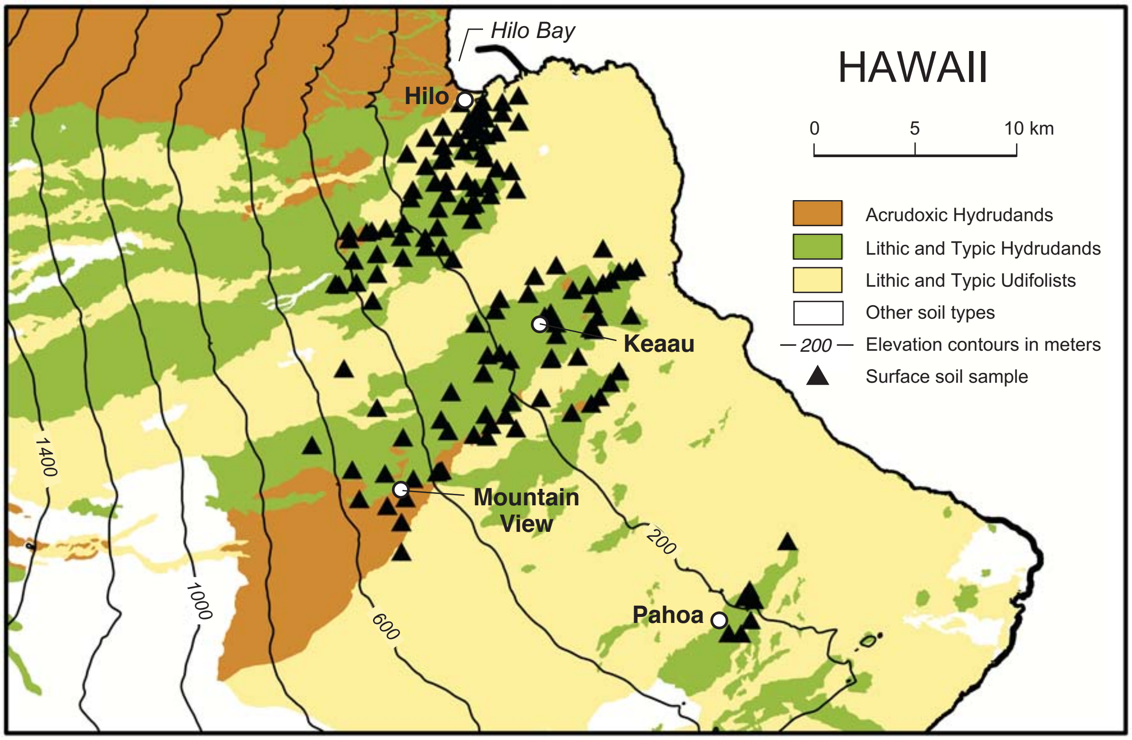
Appendix B

Supplemental Figures



Appendix Figure B.1. Photographs of historical arsenical herbicide application technology to suppress emergent weeds in Hawaiian sugar cane fields: (a) wagon-mounted tank for delivery of herbicides to fields for distribution to sled-based tanks or backpack sprayers, (b) sled-mounted tank for dispensing herbicide, (c) worker wearing knapsack sprayer, and (d) herbicide application gang treating weeds in young sugar cane. Photos from Larson (1914a).



Appendix Figure B.2. Location of surface soil samples within study area, Island of Hawaii, plotted over soil distribution map (Soil Survey Staff 2010). Sugar cane was primarily planted in Hydrudand soils since Udifolist soils, developed in young basalt lava flows, were not developed sufficiently to support cultivation.

Appendix C

Supplemental Tables

Table C.1. Comparison of *in vitro* assay methods,[a] Olaa Series Hydrudands, Keaau, Hawaii.

Sample [b]	As_{TOT} [c] (mg kg^{-1})	PBET [d]		IVG [e]		SBRC [f]	
		As_{IVBA} (%)		As_{IVBA} (%)		As_{IVBA} (%)	
		Gastric	Intestinal	Gastric	Intestinal	Gastric	Intestinal
1	404	2.2	2.8	4.2	3.0	4.1	1.1
2	337	2.4	2.5	3.8	3.5	4.0	1.2
3	344	2.2	2.3	3.8	3.1	4.2	1.2
4	215	4.2	4.8	6.0	5.8	6.9	2.0
5	321	2.5	3.5	4.3	3.5	4.6	1.5
6	453	1.9	2.5	3.0	2.6	3.1	1.0
7	193	3.7	4.3	6.1	4.2	9.2	2.0
8	307	2.4	3.7	3.5	3.4	4.1	1.1
9	168	2.1	2.8	4.1	3.0	3.6	1.1
10	160	1.8	3.9	3.3	2.3	3.3	1.1
11	207	1.7	1.6	2.9	2.8	2.9	0.9
12	226	2.6	3.3	3.7	3.9	4.2	1.9
13	149	3.4	3.8	5.3	4.9	6.4	1.5
14	185	1.4	2.0	2.5	4.2	2.5	0.9
15	313	2.4	2.9	3.2	1.1	4.6	1.1
16	162	1.5	2.6	2.2	1.5	2.6	1.0
17	201	1.7	1.9	2.8	1.7	3.0	0.9
18	316	1.1	1.1	1.8	1.0	1.9	0.7
19	309	1.5	2.4	2.0	2.4	2.4	0.9
20	305	1.5	3.0	2.7	3.0	3.2	1.0
Average	264	2.2	2.9	3.6	3.1	4.0	1.2
SD	88	0.8	0.9	1.2	1.2	1.7	0.4

[a] Laboratory analysis by M. Lord-Hoyle, Royal Military College of Canada, under contract to HDOH.

[b] Samples are Ap horizon soils from locations in vicinity of Keaau, Hawaii.

[c] Total arsenic by HCl and HNO_3 digestion, ICP.

[d] After method of Ruby et al. (1996).

[e] After method of Rodriguez et al. (1999).

[f] After method of Kelley et al. (2002), Drexler and Brattin (2007).

Table C.2. Comparison of targeted dissolution methods for common iron minerals.

Mineral	Formula	Percent Removal (for optimal extraction times)			
		Na Acetate[a]	HAH[b]	Dithionite[c]	Oxalate[d]
Ferrihydrite	$Fe_5HO_8{\cdot}4H_2O$	12%	99%	100%	99%
Lepidocrocite	γ-FeOOH	10%	99%	100%	100%
Akaganeite	β-FeOOH	0%	4%	100%	4%
Goethite	α-FeOOH	0%	0%	100%	1%
Hematite	Fe_2O_3	0%	0%	94%	0%
Magnetite	Fe_3O_4	0%	0%	7%	100%

Source: Poulton and Canfield (2005).

Note: Shaded values indicate near complete dissolution.

[a] Na acetate method, pH 4, 24 hr after Tessier et al. (1979).

[b] Hydroxylamine hydrochloride method after Chester and Hughes (1967).

[c] Citrate-dithionite method from Raiswell et al. (1994) after Mehra and Jackson (1960) and Lord III (1980).

[d] Ammonium oxalate method after McKeague and Day (1966) and Phillips and Lovley (1987).

Table C.3. Vertical soil profile data, eastern portion of Island of Hawaii.[a]

Depth (cm)	Horizon[b]	pH[c]	TOC[d] (g kg^{-1})	Fe_{TOT}[e] (g kg^{-1})	Fe_{HAH}[f] (g kg^{-1})	Fe_{CD}[g] (g kg^{-1})	Al_{TOT}[h] (g kg^{-1})	Si_{TOT}[i] (g kg^{-1})	P_{TOT}[j] (mg kg^{-1})	P_{CD}[k] (mg kg^{-1})	As_{TOT}[l] (mg kg^{-1})	As_{IVBA}[m] (mg kg^{-1})	As_{IVBA}[n] (%)
Lithic Hydrudands Profile (Olaa Series)													
10	Ap	5.7	123	86	11.4	30.9	58.1	132	2,340	640	330	28	8.6
20	Ap	5.9	95	96	11.9	37.6	69.3	142	2,930	740	400	29	7.2
30	Bw	5.9	97	103	14.9	49.4	70.3	135	2,470	580	660	24	3.7
40	Bw	6.0	72	109	13.9	45.0	74.1	137	1,700	360	330	14	4.3
50	Bw	6.1	70	112	9.9	46.0	80.4	135	2,010	410	180	7.7	4.3
60	Bw	6.0	94	108	14.7	53.4	69.8	120	2,420	740	440	18	4.1
80	Bw/C	5.9	82	94	9.1	33.4	84.5	125	1,390	250	95	5.6	5.9
100	C	5.8	55	68	5.0	17.2	96.0	143	1,600	190	32	1.0	3.1
120	C	5.9	40	60	3.3	9.2	90.1	148	1,120	60	21	0.6	2.8
140	C	5.9	43	57	4.5	9.6	109.4	143	1,660	ND	7.9	<1	–
Acrudoxic Hydrudands Profile (Ohia Series)													
10	Ap	5.9	86	140	20.4	107	105	80	3,140	1,150	99	1.6	1.6
20	Ap	5.8	79	146	15.5	113	108	87	2,670	1,120	36	0.7	1.9
30	Ap	5.9	82	146	23.9	107	106	83	3,040	1,270	110	2.3	2.1
40	Bw_1	6.0	51	147	13.1	103	131	62	2,030	710	49	1.0	2.1
50	Bw_1	6.0	32	140	5.0	108	138	60	1,250	480	13	<1	–
60	Bw_2	6.1	27	173	9.0	134	156	35	1,190	350	8.6	<1	–
70	Bw_2	6.1	23	188	8.6	159	153	33	1,120	290	16	<1	–
80	Bw_2	6.2	25	175	8.1	137	144	39	1,110	300	16	<1	–
90	Bw_2	6.2	25	134	7.3	124	103	43	1,090	340	9.0	<1	–

Note: TOT = total, HAH = hydroxylamine hydrochloride extractable, CD = citrate-dithionite extractable, IVBA = *in vitro* bioaccessible (SBRC-g method).

[a] < 250 μm soil fraction.

[b] Ap = A horizon, plowed; Bw = B horizon, weathered; C = weather rock.

[c] SD of replicate pH measurements is 0.10 pH units.

[d] Replicate total organic carbon measurements indicate relative error (coefficient of variance [CV]) of 0.6%.

[e] Analysis of Fe_{TOT} by acid digestion and ICP; replicate measurements indicate CV of 1.3%.

[f] Replicate measurements of Fe_{HAH} indicate CV of 7%.

[g] Replicate measurements of Fe_{CD} indicate CV of 1.2%.

[h] Analysis of Al_{TOT} by acid digestion and ICP; replicate measurements indicate CV of 1.7%.

[i] Analysis of Si_{TOT} by acid digestion and ICP; replicate measurements indicate CV of 2.1%.

[j] Analysis of P_{TOT} by acid digestion and ICP; replicate measurements indicate CV of 7%.

[k] Triplicate measurements of P_{CD} indicate CV of 8%.

[l] Analysis of As_{TOT} by acid digestion and ICPMS; replicate measurements of NIST 2710 control soil indicate CV of 6%.

[m] Analysis of As_{IVBA} by SBRC-g; replicate measurements of NIST 2710 control soil indicate CV of 9%.

[n] As_{IVBA} (percentage basis) is the As_{IVBA} in concentration form divided by As_{TOT}; replicates indicate CV of 11%.