

BIOACCESSIBLE ARSENIC IN SOILS OF THE ISLAND OF HAWAII

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Preface

The body of work contained in this dissertation was designed to further our understanding of bioaccessible arsenic in iron-rich, volcanic-derived soils of the Island of Hawaii. The work is driven by three primary research objectives, corresponding to the three chapters of this dissertation. The first is the study of the areal and vertical extent, mobility and bioaccessibility of arsenic in soils of the eastern portion of the Island of Hawaii. Elevated soil arsenic was discovered in this region several years ago, the result of historical arsenical herbicide use on sugar cane. Understanding the extent of arsenic contamination, and its associated mobility and bioaccessibility was deemed critical to our understanding of potential human direct contact hazards and risks to aquifer water quality. The second objective was to understand how arsenic contaminant levels and various soil properties affect the degree of arsenic bioaccessibility. This type of research had previously been performed for various soil types in North America and Australia, but never for volcanic-derived Andisols prevalent on the Island of Hawaii. The final objective was to investigate in-situ remediation technologies for reducing arsenic bioaccessibility in soils, by way of iron amendments designed to bind arsenic, making it less bioaccessible.

The format of this dissertation consists of three chapters, following the principal study objectives outline above. Each chapter is constructed as a nearly independent manuscript, with little cross reference to other chapters. This format was selected in order to facilitate the preparation of journal-ready manuscripts upon completion of work. Because of this format, some of the material may appear repetitive across chapters – for example the Methods sections of each paper will contain a similar description of the *in vitro* bioaccessibility test used throughout the body of work. In addition, each chapter has its own Abstract, References, Tables and Figures. A Dissertation Abstract is provided to summary the entire body of work.

Bioaccessible Arsenic in Soils of the Island of Hawaii

Abstract

Arsenical herbicides were used extensively in sugar cane cultivation across the eastern portion of the Island of Hawaii. As a result, surface soil arsenic concentrations are ubiquitously elevated, averaging 260 mg kg^{-1} in former plantation soils. Arsenic (As) has migrated downward in the soil profile to depths of 50-80 cm, however, to date no As has been detected in groundwater wells within the study area (or elsewhere in Hawaii). Pedogenic solid phases in these Hydruclands, consisting of iron oxyhydroxides, allophane-like aluminosilicates, and metal-humus compounds, strongly adsorb As. *In vitro* As bioaccessibility ranges from <1 to 52 percent of total As. Risks to human health by direct contact (soil ingestion) are significantly reduced by low As bioaccessibility in Hydruclands; however some of the former sugar cane plantation soils likely have bioaccessible As (AS_{BAC}) exceeding Hawaii Department of Health action levels, and will require mitigating actions.

Total As and key soil properties including pH, total organic carbon, total Fe, and reactive (citrate-dithionite (CD) and hydroxylamine hydrochloride extractable) Fe, Al, Si and P concentrations, were evaluated by multivariate linear regression modeling to predict AS_{BAC} . Two predictor variable models, with total As as the first predictor and either total Fe, CD-extractable Fe, or CD-extractable Al, as the second predictor, were able to explain 85-86% of the variability (R^2) in AS_{BAC} .

Ferric chloride plus lime and ferrous sulfate plus lime were applied to As-contaminated soils in a field plot setting to determine the potential for reducing AS_{BAC} by formation of additional Fe oxyhydroxide substrate. The two Fe sources performed similarly in reducing AS_{BAC} over the 2 year observation period, with 30-41% reduction in AS_{BAC} for 0.25 wt % Fe dosing (dry soil basis) and 59-63% reduction for 0.5 wt % Fe dosing. The cost of in-situ treatment of As-contaminated soil with ferrous sulfate plus lime to lower AS_{BAC} is estimated to be an order of magnitude less than excavation and landfill disposal on the Island of Hawaii, making the technology a viable remedial alternative when remedial action objectives are based on AS_{BAC} levels.

Table of Contents

Bioaccessible Arsenic in Soils of the Island of Hawaii	iii
Abstract	iii
List of Tables.....	vii
List of Figures	viii
Chapter 1. Bioaccessibility of Anthropogenic Arsenic in former Sugar Cane Lands, Island of Hawaii.....	1
Abstract	1
1.1 Introduction.....	2
Problem definition and study objectives	2
Study area and use of arsenical herbicides	3
Geology, soils and sugar cane plantation development.....	4
1.2 Methods.....	6
Sample collection and laboratory preparation.....	6
Mineralogical assessment.....	6
Elemental analysis	7
Arsenic sorption isotherms	8
<i>In vitro</i> bioaccessibility test method.....	8
Arsenic speciation.....	9
Targeted dissolution of ferric iron substrate.....	10
1.3 Results and Discussion.....	11
Mineralogy.....	11
Major element content.....	12
Arsenic speciation and association with solid phases	14
Arsenic sorption properties on Hydrudands	15
Arsenic distribution in surface soils	16
Vertical extent of arsenic in Hydrudands	16
Bioaccessible arsenic in surface soils and vertical profiles.....	19
1.4. Bioaccessible Arsenic and the Need for Mitigating Actions	20
1.5. References	21

Chapter 2. Soil Properties and their Influence on Arsenic Bioaccessibility	55
Abstract	55
2.1 Introduction	55
Previous Studies of Controls on Arsenic Bioaccessibility	57
Solid-phase Properties of Hawaiian Andisols	58
Sorption and Sequestration of Arsenic in Soil.....	58
Objective of Current Study.....	60
2.2 Methods.....	61
Study Area Soils, Collection and Laboratory Preparation	61
<i>In vitro</i> Bioaccessible Arsenic.....	61
Analysis of Soil Chemical Properties.....	63
2.3 Results and Discussion.....	63
Soil Properties and Analysis of Extent of Soil Weathering.....	63
Observed Arsenic Contaminant Loading	65
Controls on Bioaccessible Arsenic.....	65
Comparison with Other Modeling Studies	67
Effect of Total Arsenic Loading and Reactive Fe Content on Bioaccessible Arsenic	68
Streamlining Investigations of Bioaccessible Arsenic	70
2.4 Conclusions	70
2.5 References	72
Chapter 3. Iron Amendments to Reduce Bioaccessible Arsenic	96
Abstract	96
3.1 Introduction	96
Problem Definition, Objectives	96
Previous Studies to Reduce Bioaccessible Arsenic.....	97
3.2 Materials and Methods	98
Study Soils.....	98
Bioaccessible Arsenic Testing.....	99
Laboratory Treatability Testing.....	99
Field Plot Study	100

Targeted Extractions, pH and Redox Measurements	100
Phosphate Amendments of Fe-treated Soils.....	101
X-ray Adsorption Spectroscopy	101
3.3 RESULTS.....	102
Laboratory Treatability Testing.....	102
Field Plot Study	102
X-ray Absorption Spectroscopy Results.....	104
Targeted Extractions, pH and Redox Measurements	104
Phosphate Amendments	104
3.4 Discussion	105
Formation of Fe Substrate	105
Arsenic binding to Fe Substrate.....	106
Potential Full-scale Implementation.....	106
Conditions Potentially Increasing Bioaccessible Arsenic	107
3.5 Conclusions	108
3.6 References	109

List of Tables

Chapter 1

Table 1.1	Soil analysis methods.....	29
Table 1.2	Comparison of in vitro bioaccessibility test methods in Typic Hydrudands ...	30
Table 1.3	Major element composition of Kau Basalt and overlying soils.....	31
Table 1.4	Total arsenic in surface soils of former sugar cane planting areas	32
Table 1.5	Vertical soil profile data.....	33
Table 1.6	Total and bioaccessible arsenic in surface soils.....	34

Chapter 2

Table 2.1	Comparison of targeted dissolution techniques for common iron minerals	78
Table 2.2	Targeted iron mineral dissolution methods.....	79
Table 2.3	Soil properties, <0.25mm fraction, air-dried basis	80-82
Table 2.4	Linear regressions to predict bioaccessible arsenic	83

Chapter 3

Table 3.1	Test plot soil properties.....	112
Table 3.2	Bench-scale Fe amendment treatability study results.....	113
Table 3.3	Field plot Fe amendment treatability study results.....	114
Table 3.4	Field plot, replicate sampling data and summary statistics.....	115
Table 3.5	Field plot, replicate sampling data, Student's t-test.....	116
Table 3.6	Structural parameters from XAFS analysis	117
Table 3.7	Soil properties, 336 days post treatment.....	118
Table 3.8	Phosphate amendment study results	119

List of Figures

Chapter 1

Figure 1.1	Location of sugar cane cultivation on Island of Hawaii, circa 1937	35
Figure 1.2	Current towns and former sugar cane plantations within study area	36
Figure 1.3	Photographs of arsenical herbicide equipment and application, 1914.....	37
Figure 1.4	Geologic map with surface soil arsenic concentrations.....	38
Figure 1.5	Map of soil types with surface soil arsenic concentrations.....	39
Figure 1.6	TEM photomicrographs	40
Figure 1.7	Comparison of Kau Basalt and soil major element concentrations	41
Figure 1.8	Ca/Ti ratio versus total Fe content for Kau Basalt and soils.....	42
Figure 1.9	EDXRF spectra of Kau Basalt and soils	43
Figure 1.10	Soil particle size fractionation and total arsenic content	44
Figure 1.11	Microprobe data for secondary minerals, As versus Fe/Fe+Al	45
Figure 1.12	XANES spectra of Hydrudands compared to arsenic standards.....	46
Figure 1.13	Arsenate kinetic sorption isotherm for Typic Hydrudands.....	47
Figure 1.14	Arsenate equilibrium isotherms for Typic and Acrudoxic Hydrudands.....	48
Figure 1.15	Soil arsenic concentrations across the former Ola‘a Sugar Plantation	49
Figure 1.16	Photographs of Typic and Acrudoxic Hydrudands soil profiles.....	50
Figure 1.17	Vertical soil profile data for Typic Hydrudands	51
Figure 1.18	Vertical soil profile data for Acrudoxic Hydrudands	52
Figure 1.19	Cross-plot of total and bioaccessible arsenic, surface soils	53
Figure 1.20	Cross-plot of bioaccessible arsenic and Ca/Ti ratio.....	54

Chapter 2

Figure 2.1	Cross-plot of total Fe versus citrate-dithionite extractable Fe	84
Figure 2.2	Major and trace elements in soils compared to parent basalt composition...85	
Figure 2.3	Cross-plot of Ca/Ti ratio to citrate-dithionite extractable Fe.....	86
Figure 2.4	Cross-plot of total arsenic to bioaccessible arsenic	87
Figure 2.5	Predictions of bioaccessible As from total As and CD-extractable Fe	88
Figure 2.6	Comparison of observed As_{BAC} to Yang et al. (2002) predicted values	89

Figure 2.7	Comparison of observed As_{BAC} to Juhasz et al. (2007a) predicted values ...	90
Figure 2.8	Soil properties from Yang, Juhasz and current studies.....	91
Figure 2.9	Cross-plot of total As versus bioaccessible As, chemical release site.....	92
Figure 2.10	Arsenic sorption isotherms	93
Figure 2.11	Reactive Fe content and its affect on predicted bioaccessible As	94
Figure 2.12	Total arsenic loading and its affect on predicted bioaccessible As	95

Chapter 3

Figure 3.1	Bioaccessible arsenic in amended and control soils	120
Figure 3.2	Bioaccessible Fe in amended and control soils.....	121
Figure 3.3	XANES spectra for $FeCl_3$ -treated and control soils	122
Figure 3.4	XAFS radial structure functions	123
Figure 3.5	Effect of phosphate amendment on bioaccessible arsenic.....	124
Figure 3.6	Effect of phosphate amendment on bioaccessible P	125
Figure 3.7	Eh-pH diagram of common Fe oxides, with test plot soils.....	126

Chapter 1. Bioaccessibility of Anthropogenic Arsenic in former Sugar Cane Lands, Island of Hawaii

Abstract

Arsenical herbicides were used extensively in sugar cane cultivation across the eastern portion of the Island of Hawaii. As a result, surface soil arsenic concentrations are ubiquitously elevated, averaging 260 mg kg^{-1} in former plantation soils across more than 60 km^2 of former agricultural land. Sodium arsenite solution was sprayer applied for emergent weed control in cane fields from 1913 to about 1950, and arsenic has migrated downward in the soil profile to depths of 50-80 cm, presumably by both physical mechanisms (cultivation tillage and plant root bioturbation) and by dissolved or colloidal transport within the soil solution. Formerly cultivated soils are of the Hydrudands great group of the Andisol soil order, formed from the weathering of basaltic lava and tephra 3,000 to 30,000 yr old. A continuum of soil compositions reflects a range of parent material contributions from lava rock to ash, and differential weathering of the soil profile. Pedogenic solid phases consist of short-range order materials, principally iron oxyhydroxides, allophane-like aluminosilicate compounds, and metal-humus compounds. These reactive solid phases, prevalent in volcanic tephra-derived soils, strongly adsorb oxyanions, such as phosphate and arsenite/arsenate. The most weathered subgroup of Andisols, Acrudoxic Hydrudands, contains more reactive secondary solid phase materials than less weathered Typic and Lithic Hydrudands. Acrudoxic Hydrudands show higher arsenate sorption capacity in equilibrium sorption isotherms. High arsenic sorption capacity limits desorption and vertical migration and prevents contamination of the underlying groundwater aquifer, despite high arsenic loading and precipitation rates. To date, no arsenic has been detected in groundwater wells within the study area (or elsewhere in Hawaii). *In vitro* arsenic bioaccessibility of study soils, as measured by the SBRC gastric-phase test, ranges from 2 to 35 percent and averages 9 percent of total arsenic. The percentage of bioaccessible arsenic is highest in less weathered soils with high lithic content (Udifolists, Typic and Lithic Hydrudands), and lower in more weathered ash-dominant soils (Acrudoxic Hydrudands) with higher reactive Fe content. One Typic Hydrudands from the study area has been tested by others for both *in vivo* relative bioavailability (cynomolgus monkey model) and *in vitro* bioaccessibility (SBRC method), yielding $5 \pm 2\%$ relative arsenic bioavailability and 6.5% arsenic bioaccessibility, respectively. Risks to human health by direct contact (soil ingestion) are significantly reduced by low arsenic bioaccessibility in Hydrudands; however some of the former sugar cane plantation soils likely have bioaccessible arsenic exceeding Hawaii Department of Health risk-based concentrations, and will require mitigating actions.

1.1 Introduction

Problem definition and study objectives

Arsenic (As) contaminated soil is an emerging environmental issue in 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) identified As contamination of soil in the vicinity of Kea'au, Hawaii in the eastern portion of the Island of Hawaii, believed to have been caused by historical arsenical herbicide use in former sugar cane cultivation (HDOH, 2007a). Although no evidence of human health impacts from exposure to As-contaminated soil were identified in the Kea'au vicinity (ATSDR, 2007), properties containing As above regulatory-defined risk-based concentrations across Hawaii require investigation, remediation, and placement of long-term land use restrictions (HDOH, 2006; 2010). The full extent of As soil contamination in Hawaii is currently unknown.

Incidental ingestion of soil with elevated As levels could potentially present a human health risk, especially to sensitive populations such as children. The bioavailability of metals and metalloids in soil, sediment and solid waste is often considered in the estimation of potential human health risk. Not all As in soil is bioavailable, especially in soils or soil-like media that have strong As binding capacity, such as the iron-rich volcanic-derived soils of Hawaii. USEPA (2007) and other environmental regulatory agencies have recognized the importance of considering the degree of bioavailability of metal contaminants in risk assessments and remedial action evaluations. The relative oral bioavailability of soil As in animal models (monkey and juvenile swine) has been shown to be highly variable and in part controlled by soil mineralogy and geochemical conditions (Roberts et al., 2007; Juhasz et al., 2007). Bioavailability of As in soil is primarily a function of As speciation and solid-phase associations (Scheckel and Chaney, 2009).

Oral bioaccessibility is defined as the fraction of a substance that is soluble in the gastrointestinal system and is available for absorption (Paustenbach, 2000). *In vitro* bioaccessibility assays, with proper validation, can be used as a predictor of relative oral bioavailability of metal(loid)s (Ruby et al., 1996). In lieu of costly animal studies of relative As bioavailability, a number of 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 As extracted in these *in vitro* tests is termed bioaccessible arsenic (AS_{BAC}) (Ruby et al., 1996). *In vitro* bioaccessibility may be a suitable predictor of relative As bioavailability (USEPA, 2007), particularly when validated with an *in vivo* animal study. Due to the complexity of chemical contaminants in soil substrates, multiple tools, including *in vitro* bioaccessibility assessments, are useful in supporting human exposure assessments (Schoof, 2004). The HDOH (2006,

2010) recommends the use of As_{BAC} , not total As, in evaluation of potential human health risk and need for remedial action at sites with As-contaminated soil.

Initial studies of As-contaminated soil in the vicinity of the town of Kea'au (HDOH, 2007a) showed total As (As_{TOT}) levels of 55 to 629 mg kg⁻¹, with *in vitro* As_{BAC} ranging from 1 to 18 percent of As_{TOT} . Given the uncertainties in the extent of elevated soil As, and the variability in observed bioaccessibility, further study was warranted. Objectives of the current study¹ were to determine: 1) the areal and vertical extent of As in former sugar cane soils of the eastern portion of the Island of Hawaii, 2) the speciation of As and its solid-phase associations, and 3) the degree of bioaccessibility and potential mobility of soil As in these soils.

Study area and use of arsenical herbicides

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 1800's until the late 1900's. Plantations were established in most areas where soil development was sufficient, below elevations of 600 m above mean seal level (MSL). 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 1.1). South of Hilo Bay, sugar was cultivated in discontinuous parcels defined by older lava flows with adequate soil development. The current study area extends from Hilo Bay southeast 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 was located immediately south and southwest of Hilo, and operated from 1879 to 1947. The Ola'a Sugar Company plantation (later called Puna Sugar Company) operated from 1900 to 1982, consisting of contiguous plantation lands extending from the towns of Kea'au to Mountain View, with isolated plantings further south to the Town of Pahoa (Figure 1.2). Sugar cane cultivation reached its full historic extent by the 1920's (Territory of Hawaii, 1939; Dorrance and Morgan, 2000), extending across approximately 60 km² (6000 hectares) within the study area. Sugar cultivation in the Waiakea plantation ceased in 1947, and the Town of Hilo expanded across former cane lands. At higher elevations above Hilo, and across much of the former Ola'a plantation, current land use consists of diversified agriculture (papaya, macadamia nuts, and ornamentals), low-density residential development and fallow land.

The use of As for chemical weed control in sugar cane cultivation in Hawaii was first implemented in 1913 at the Ola'a plantation (Larsen, 1914a), and eventually expanded to other plantations in 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

¹ The current study refers to Chapter 1 of this dissertation.

by farm workers using sled or knapsack sprayers (Larsen, 1914b; Hance, 1938). The sodium arsenite herbicide was sprayed on emergent weeds beneath growing sugar cane, with 2 to 4 applications over the two-year cane growing period. Photographs of As application equipment and techniques from 1914 at the Ola'a Sugar Plantation are provided in Figure 1.3. By the 1940's, arsenical herbicides were replaced by synthetic organic herbicide compounds (Pentachlorophenol [PCP] and 2,4-Dichlorophenoxyacetic acid [2,4-D]), and the widespread use of arsenical herbicides ceased (Hance, 1948; Hanson, 1959).

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

Geology, soils and sugar cane plantation development

Geology

The Hawaiian Islands are a chain of volcanic islands formed from historical and ongoing basaltic eruptions. Sugar plantations in the eastern portion of the Island of Hawaii, from Hilo Bay southward, developed in soils formed above shield-building lava flows sourced from the Mauna Loa and Kilauea volcanoes to the west (Figure 1.1). Flows from Mauna Loa are assigned to the Kau Basalt series, whereas those from Kilauea are called the Puna Basalts (Stearns and Macdonald, 1946). The basalts are composed dominantly of plagioclase, pyroxene, and olivine, with lesser amounts of magnetite, ilmenite and apatite (Macdonald, 1949). Kau and Puna basalts are dominantly tholeiitic a'a and pahoehoe flows, with variable amounts of olivine, plagioclase and pyroxene phenocrysts. Tephra deposits, dominantly composed of ash and lapilli, are intercalated with basalt flows, and have been sourced from Mauna Kea, Mauna Loa and Kilauea (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 (Figure 1.4). 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 750 yr to more than 11,000 yr; whereas Puna Basalts from Kilauea range from recent to 3,000 yr. There has been significant tephra deposition within the study area, including the Uwekahuna Ash Member of the Puna Basalt, which was deposited as fallout that occurred dominantly northeast of Kilauea between approximately 2000 and 2800 yr (Dzurisin et al., 1995).

Soils

Soils have developed to varying degrees in emplaced basalt lava. Deeper soils are present in older flows due to successive accumulation of tephra, whereas shallow incipient soils occur in recent flows². Soil development sufficient to support sugar cane cultivation is generally restricted to areas with lava flows of age exceeding 3,000 yr. These soils are of the Andisol soil order, derived from young basaltic volcanic lava rock and tephra, with contributions of organic matter and atmospheric dust. Soils in lava flows younger than 3,000 yr are either shallow, immature Andisols or Histosols, and were not sufficiently developed to support cane cultivation.

Within the study area, soils of two taxonomic great groups are present: Hydrudands and Udifolists (USDA-NRCS, 2010). The spatial distribution of soil types (Figure 1.5) is largely controlled by the underlying geology (Figure 1.4). Hydrudands are Andisols with high water retention capacity (1500 kPa water retention >100%), typically formed in volcanic ash soils. Several Subgroups of Hydrudands are present: Acrudoxic Hydrudands are highly weathered with low extractable base content, present as deep soils (>1m thickness) developed in lava flows more than 10,000 y old. They are dominated by weathered ash components, and contain a small fraction of entrained lithics (weathered basalt rock fragments). The Acrudoxic Hydrudands have a limited areal distribution within the study area (Figure 1.5), but were optimal soils for sugar cane cultivation because of their depth and ease of tillage. Typic and Lithic Hydrudands are developed in lava flows 3,000 to 10,000 y old, and are less weathered than Acrudoxic Hydrudands. They are generally <1 m in thickness, and have appreciable lithic content (greater than 35 percent rock fragments). The majority of 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 1,500 yr 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 Al and Fe (USDA-NRCS, 2006). Pedological, geochemical and ecological controls on long-term soil development in tephra-derived soil of Hawaii have been studied at a chronosequence of sites with substrates ranging from 300 y to 4.1 my old (Crews et al., 1995; Vitousek et al., 1997; Chorover et al., 2004). 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 my or more. Formation of crystalline clays and sesquioxides occurs in Hawaii's oldest soils (Vitousek et al., 1997).

² Information on soils is from USDA-NRCS (2010), whereas geology and age of lava flows are from Wolfe and Morris (1996).

Sugar Cane Plantation Development

The sugar plantations in the study area were developed in Hydrudands at elevations of 20-600 m MSL, with mean annual temperature of 20.5°C and annual rainfall of approximately 4000 mm (Giambelluca et al., 1986). The location of former cane cultivation can be determined from historical maps (Cook, 1926; Williams, 1933; Territory of Hawaii, 1939), aerial photographs and U.S. Geologic Survey 7.5-Minute Series topographic maps. The bulk of the plantings for the Waiakea and Ola'a plantations were within two contiguous tracts of land (Figure 1.2), however several isolated areas of Hydrudands soils, surrounded by young lava flows and associated Udifolist soils, called "kipukas" in the Hawaiian language, were also placed in cane production.

1.2 Methods

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

Sample collection and laboratory preparation

Surface soils were collected from 90 spatially-distributed locations within and beyond the former Waiakea and Ola'a plantation boundaries, in order to map the aerial extent of elevated soil As occurrence and for further laboratory analyses (Table 1.1). At each sample location, soil was collected from an approximate 0.1 m² area from the 0-20 cm depth interval, excluding plant litter. Test pits were excavated at several locations to assess vertical soil profiles. Within 1-1.5 m deep pits, composite samples were collected from sidewalls at discrete depth intervals (10 or 20 cm intervals). A portable energy dispersive X-ray fluorescence (EDXRF) instrument was used during field sampling activities for screening of soil As content.

Soil samples were air dried for 7 to 10 days, until daily moisture loss was less than 1% ,and sieved to <2 mm grain size ("soil fraction") using a multi-increment subsampling procedure (Gerlach and Nocerino, 2003). A "fine fraction" (<0.25 mm) was prepared for *in vitro* analysis of As_{BAC}. USDA-NRCS (2004) uses the <2 mm grain size fraction for analysis of most soil properties, whereas the <0.25 mm fraction is used for evaluation of As bioavailability and bioaccessibility. Soil fraction and fine fraction materials were oven dried (105°C) and fine ground for elemental analysis by XRF or acid digestion/inductively coupled plasma (ICP) spectrometry. Subsamples for analysis were collected using a rotary riffler splitter or by multi-increment subsampling procedures. Field moist samples were separated into grain-size fractions by wet sieving with distilled water, and then air dried prior to total As analysis by acid digestion/ICP.

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 (less than 10 μm particle sizes) was inspected by transmission electron microscopy (TEM) to determine secondary mineral phases based on morphology, internal structure and electron transmissivity. Field moist soil samples were prepared by wet sieving with deionized water followed by gravity settling and centrifugation; the finest solids were applied to lacey Formvar® grids and inspected on a Zeiss Leo 912 energy filtering TEM.

Elemental analysis

Elemental analysis of soils was performed using X-ray fluorescence (XRF), electron microprobe and acid digestion/ICP spectrometry methods. Whole soil (<2 mm fraction) major element analysis was performed on a diverse subset of study area soils (N=32) on the University of Hawaii Siemens 303 AS XRF spectrometer using a rhodium-target, end-window X-ray tube. Soils were oven dried (105°C), ground to powder in an alumina swing mill, then combusted at 750°C to remove water and organic compounds (loss on ignition [LOI] recorded). The resulting solids were representative of anhydrous mineral solids. Powders were melted with the aid of a lithium tetraborate flux and formed into fused-glass disks. Sample preparation followed methods similar to those of Norrish and Hutton (1977). Corrected intensities were calibrated against a wide range of natural rock standards. Accuracy and precision data for this system are reported in Sinton et al. (2005). Duplicate analyses were run for all samples, and a subset of samples (N=7) were run in replicates of 3 or 4 for determination of analytical variance. Replicate analysis results were averaged, reported as weight percent oxides and normalized to 100 percent. Elemental concentrations were derived from normalized oxide concentrations, reported as zero-moisture concentrations or as oven-dried (105°C) concentrations by correction for LOI.

Various soil preparations were analyzed with a Bruker Tracer III-V portable EDXRF instrument utilizing a rhodium-target X-ray tube and Al/Ti filters. Raw spectra were collected over 300 s acquisition time and processed using Bruker Artax software for removal of background. Calibration curves were developed for major and trace elements (Ca, Ti, Fe, Sr, Zr) using Hawaiian soils analyzed by acid digestion and ICP. Arsenic was determined using site-specific standard reference materials (SS-SRMs), prepared by spiking study soils with a sodium arsenate solution at a range of known As concentrations. Separate As SS-SRMs were prepared for low and high Fe soils, to allow correction of As fluorescence due to absorption by matrix Fe content (the dominant contributor to sample atomic density). Soils for SS-SRMs contained less than 10 mg kg^{-1} As_{TOT} and were collected from locations that had not been cultivated for sugar cane.

Electron microprobe wavelength dispersive spectrometry (WDS) was used to determine the elemental composition of secondary mineral phases containing As. Soils were evaluated using polished grain mounts on a JEOL JXA-8600 probe at the University of Colorado Laboratory for Environmental and Geological Studies (LEGS). Secondary

solid phase materials were identified in backscatter images, and analyzed for elemental composition in WDS mode at an accelerating voltage of 15 kV, 20 nA beam current and an approximate beam diameter of 1 μm . Fluorescence was calibrated using standard reference minerals, and intensities and concentrations were reported after matrix corrections.

Total elemental analysis was conducted on select soils, in particular samples from the vertical soil profiles, using a three acid digestion (similar to EPA Method 3052) with analysis on a Varian Vista MPX ICP optical emission spectrophotometer (ICPOES). Between 100-150 mg of finely-ground oven-dried soil sample was digested in 5 ml concentrated HNO_3 , 2 ml HCl and 2 ml of HF , followed by microwave heating to 180°C for 20 min. After cooling the contents were transferred to polyethylene bottles along with 50 ml of 0.50M boric acid solution, and diluted to ~100 grams with 18 mega-ohm deionized water. This resulting solution was analyzed by ICPOES.

Arsenic sorption isotherms

Arsenic sorption isotherms were prepared using the method of Fox and Kamprath (1970). The batch sorption tests consisted of 4 g of <2mm air-dried soil in 40 mL of 0.01M CaCl_2 solution containing dissolved sodium arsenate heptahydrate, run in 50 mL polyethylene centrifuge tubes, rotated in a water bath at 25°C for 7 days. At completion of the sorption test, tubes were centrifuged for 10 minutes at 2000 g and supernatant filtered through a $0.45\mu\text{m}$ polypropylene filter. Concentrations of As in the supernatant were determined by ICP mass spectroscopy (ICPMS), and sorbed As was determined by As loss from the supernatant. Fox and Kamprath (1970) used a 6-day period for P equilibrium isotherms. This duration was evaluated for As sorption by performing a 7-day kinetic isotherm on a Typic Hydrudands soil, with an As spike concentration of 200 mg kg^{-1} . For development of this kinetic sorption isotherm, batch tests were conducted in triplicate for each of 8 time steps. Equilibrium isotherms were then developed for Acrudoxic Hydrudands and Typic Hydrudands soils with varied As solution spiking concentrations, in $10^{0.5}\text{ mg L}^{-1}$ increments, from $10\text{-}1000\text{ mg L}^{-1}$. Duplicate tests were performed for 100 mg L^{-1} spikes on each soil to assess variance.

***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) 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 we have selected the gastric phase of the SBRC test (SBRC-g) for several reasons. In a comparison study of PBET, IVG and SBRC methods for a suite of 20 soils from locations in Kea'au vicinity, within 1 km of the study test plot (HDOH,

2007b), the SBRC-g *in vitro* method generated the highest As_{BAC} values (percentage basis) of all methods (Table 1.2). Use of the SBRC-g method for determining As_{BAC} in these soils is considered “conservative” relative to other gastric and intestinal phase *in vitro* test methods, since it provides the highest estimate of As_{BAC} and therefore minimizes the potential for a type II error, such as failing to identify a potential health risk when an actual risk is present. Secondly, in a study by (Juhasz et al. 2009), four *in vitro* methods (PBET, IVG, SBRC and DIN [DIN, 2000]) were compared with *in vivo* (swine) relative As oral bioavailability for a suite of contaminated soils. The authors determined that the SBRC-g best predicted *in vivo* relative As oral bioavailability.

The SBRC-g *in vitro* test consists of extraction of 1 g of <250 μm air-dried (or oven dried $\leq 40^\circ\text{C}$) soil by 100 mL of glycine-buffered HCl at pH 1.5, conducted in a 125 mL polyethylene bottle rotated in a 37°C water bath for 1 hr. 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 As by ICPMS. Quality assurance/quality control procedures include blanks (raw extractant, no soil), blank spikes (extractant with As spike, no soil), matrix spikes (soil spiked with As), duplicate samples and control soil analyses (Drexler and Brattin, 2007). A second aliquot of soil is evaluated for As_{TOT} using acid digestion, such as EPA method 3050B (hot plate $\text{HNO}_3\text{-HCl}$), 3051A (microwave $\text{HNO}_3\text{-HCl}$) or 3052 (microwave $\text{HNO}_3\text{-HCl-HF}$), followed by ICPMS analysis of the acid extract. The percentage of bioaccessible arsenic ($As_{BAC}\%$) is the mass of dissolved As in the *in vitro* extract divided by mass of As_{TOT} in the test soil times 100 (equation 1). The concentration of As_{BAC} is the mass of dissolved As in the *in vitro* extract divided by the mass of test soil (equation 2).

$$As_{BAC}\%(\%) = \frac{\text{In vitro As (mg)}}{\text{Total As in soil (mg)}} \times 100 \quad (1)$$

$$As_{BAC} (\mu\text{g g}^{-1}) = \frac{\text{In vitro As (mg)}}{\text{Soil (kg)}} \quad (2)$$

Arsenic speciation

Soil As speciation was determined by X-ray absorption near-edge structure (XANES) analysis. A sample of Typic Hydrudands from near Kea’au was collected in field moist state under a nitrogen atmosphere (using a nitrogen-gas-filled glove bag sealed to the ground surface), frozen and transported to Stanford Synchrotron Radiation Laboratory (SSRL) for XANES evaluation as described in (Root et al., 2007). At SSRL, samples were transferred to Kapton tape in a N_2 glovebox. Arsenic K-edge spectra were collected on SSRL beamline 11-2 at a beam energy of 80-100mA, using a Ge detector and Si(220) monochromator crystal, with samples held in a liquid-He cryostat ($5\text{-}20^\circ\text{K}$). 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 As species identification.

Targeted dissolution of ferric iron substrate

The subset of surface and test pit soils analyzed for As_{BAC} were evaluated for reactive Fe, Al, Si and P content 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 the pedogenic (secondary) solid phase materials, which tend to be reactive toward sorption of oxyanions such as arsenite/arsenate.

Extractions were performed on the same $<0.25\text{mm}$ air dried soil that was evaluated by SBRC-g. Reactive Fe was determined by two extraction methods. The first consisted of extraction with 1M hydroxylamine hydrochloride 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 15 ml polyethylene centrifuge tube with 10 mL of extractant and shaken continuously for 48 h. The second reactive Fe extraction method utilized dithionite in 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) extractant 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 2000 g and supernatant was decanted and filtered through a $0.45\ \mu\text{m}$ polypropylene filter. Filtrate was analyzed for Fe, Al and Si by ICPOES. Subscripts HAH and CD are used to indicate the element content extracted by each these two operationally-defined methods (i.e. Fe_{HAH} , Fe_{CD}).

Poulton and Canfield (2005) compared the efficacy of various targeted extraction techniques for selective dissolution of common Fe minerals. Their work demonstrated that the citrate-dithionite method provided the most complete dissolution of secondary Fe minerals (ferrihydrite, lepidocrocite, goethite and hematite), whereas hydroxylamine hydrochloride targeted only the most reactive Fe forms, ferrihydrite and lepidocrocite. These extraction methods also dissolve some fraction of reactive Al and Si in soils; however we are not aware of a comparative assessment of dissolution efficacy for specific Al-oxide and aluminosilicate mineral forms as performed by Poulton and Canfield for Fe oxides/oxyhydroxides. Phosphorus was analyzed in citrate-dithionite extractions to measure the potentially reactive fraction associated with the pedogenic iron oxyhydroxide phases. Further description of targeted dissolution methods and details on reactive Fe targeted extraction methods are provided in Chapter 2.

1.3 Results and Discussion

Mineralogy

The fine silt and clay fraction (less than 10 μ m) of Ap and Bw horizons of Typic Hydrudands soils were examined by TEM to identify dominant secondary solid phases based on surface morphology, internal microstructure and electron transmissivity. Dominant solid-phase materials observed in study soils are finely-crystalline iron oxyhydroxides and aluminosilicates (allophane and imogolite) and non-crystalline gel materials. Less abundant phases included layer silicates (halloysite, smectite), opaline silica, and partially-weathered volcanic glass. Figure 1.6a shows finely-crystalline iron oxyhydroxides (ferrihydrite-like) with discrete aggregates 10-20 nm in diameter. More typical ferrihydrite morphology consists of very fine crystalline aggregates, 1-10 nm in diameter. An example of finely-crystalline ferrihydrite, with poorly ordered goethite (presumably forming from a ferrihydrite precursor) is shown in Figure 1.6b. Gels are prevalent in Hydrudands (Jones and Fox, 1978), commonly observed as coatings and binding agents for soil aggregates (Figure 1.6c). Gels are typically more electron transparent than iron oxides, alluding to lower atomic density and prevalence of Al, Si and humus content. Allophane-like aluminosilicate materials are very abundant in study soils, typically exhibiting moderate to high electron transmissivity and a short-range-order structure composed of 1-5 nm spherules aggregated in clusters or short linear patterns. Well formed imogolite, with its distinct thread-like morphology (Figure 1.6d) is less common than the more sucrosic “allophane” textures, and was only observed in subsurface soils with lower humus content. Platy layer silicates with high electron transmissivity were abundant in some samples, and may be a transition phase between gels and more structured layer silicate. In general, short-range order materials - ferrihydrite, allophane-like materials and gels - dominate 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 (Figure 1.6e)) - are observed along with significant quantities of the short range order phases. The increased crystallinity of solid phases in deeper/older soils is believed to be the result of less humus impeding crystal arrangement and more time for 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 Fe and Al 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 Fe and Al 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 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. Al-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 Al-rich allophanes with 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 Al, Fe and Si 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 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. Surface soils (N=32) were evaluated for major element composition by WDXRF, 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 (Figure 1.7). Of the major elements sourced by the parent basalt rock, Al, Ti, Mn and Fe accumulate, whereas Si, Na and Ca become depleted.

Previous studies have 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 Na and Ca loss, and Ti 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 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 Fe content, which increases as soils weather (Figure 1.8). During parent rock and soil weathering, Ca and other

nonhydrolyzing cations (Na and Mg) are depleted by weathering, whereas Fe, Al and Ti accumulate by forming relatively immobile oxides and complexing with humus (Chorover et al., 2004). We find that the Ca/Ti ratio is a useful indicator of the degree of soil weathering in study area soils, and can be evaluated in both the field and laboratory by EDXRF; these two elements have nearby $K\alpha$ 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 (Figure 1.9).

The Ca/Ti ratio may not have broad application beyond young Histosols and Andisols, as Ca can be nearly completely depleted in older soils. In addition, Ca may be magnified in shallow soils by plant re-deposition in litterfall or anthropogenically elevated by lime application in agricultural settings. 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 (Figure 1.7 and Table 1.3). Iron in the Kau Basalt, the dominant parent rock for study area soils, averages 8.7 ± 0.3 wt% (mean \pm stdev, N=63). In incipient soils formed on basalt (Udifolists), Fe is slightly enriched at about 9.4 ± 0.6 wt% (mean \pm stdev, N=5) (concentration in mineral solids after furnace combustion which removes all water and organic compounds). In more weathered Typic and Lithic Hydrudands, Fe averages nearly twice the basalt content (13.0 ± 1.6 wt% (mean \pm stdev, N=23)), and is nearly 3-times the basalt concentration in Acrudoxic Hydrudands (22 ± 2 wt% (mean \pm stdev, N=4)), the most highly weathered soil in the study area. Weathering of basaltic parent material, lava and tephra, and subsequently formed soils, leads to progressive enrichment in Ti, Al, Fe, Mn and P; and depletion of Si, Mg, Ca, and Na. 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 underlying lava flows. Udifolists developed over the youngest lavas (<1500 y old), and exhibit elemental compositions similar to parent basalt. Soils developed over older lavas show progressive deviation from the original basalt composition. The more highly weathered state of surface soils above older flows is partially due to the age of soil solids, but 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).

Arsenic speciation and association with solid phases

Arsenic in soil, originating as an aqueous sodium arsenite solution sprayed on emergent weeds and soil, is expected to strongly adsorb to secondary (pedogenic) solid phases in volcanic-ash derived Andisols. These secondary solid phase materials are amorphous to finely crystalline Fe 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 Kea'au 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 significant As enrichment in the finest sieved fraction ($<74 \mu\text{m}$, passing 200 mesh sieve) (Figure 1.10). It is likely that As is further enriched in study soils in even finer particle size fractions. For example, Smith et al. (2009) found significant As enrichment in the finest soil fraction ($<2.5 \mu\text{m}$), coincident with increased Fe content.

Solid-phase associations of As in study soils were examined by electron microprobe WDS analysis. Two dominant end member materials containing As were identified, Fe oxides and aluminosilicates. Based on observations of solid phases by TEM, discrete domains of similar material with diameters of 100-200 nm are common (Figure 1.6). Since the microprobe beam diameter is approximate $1 \mu\text{m}$, it is likely that the electron beam is exciting areas containing more than one distinct solid phase and elemental compositions would be considered averages for that sampling domain. A cross-plot of As content versus Fe/Fe+Al (molar basis) shows a general pattern of higher As content in more iron-rich materials (Figure 1.11). Arsenic is known to adsorb to short-range order Fe oxyhydroxides (such as ferrihydrite) (Sadiq, 1995) and aluminosilicates (allophane and imogolite) (Gustafsson et al., 1998). In Hydrudands of this study, As shows a general preference for binding to Fe-rich phases, however As 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), soil was collected from a location near the town of Kea'au that had been moist for an extended period of time due to rainfall. The near-surface soil (10 cm depth) from a Typic Hydrudands (Panaewa series) was collected during the rainy season (January) from a low-lying area under 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 percent 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 As species determination (Figure 1.12). 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 anticipated, due to the well drained nature of the soil, especially for soils developed over porous a'ua lava. However, during periods of high water saturation,

reducing conditions could potentially develop within the soil profile. Water saturated 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 can be poorly drained. Reduction of As(V) to As(III), in the slightly acidic study soils (5.5 to 6.5) in the presence of poorly-crystalline Fe oxyhydroxides (ferrihydrite, goethite), is not expected to result in increased As mobility (Dixit and Hering, 2003). However, reducing conditions could lead to dissolution of Fe oxyhydroxide substrate (Pedersen et al., 2006), which could potentially lead to increased concentrations of dissolved As in the soil solution and downward migration of As within the soil column.

Arsenic sorption properties on Hydrudands

A kinetic sorption isotherm for a Typic Hydrudands was prepared, using the method of Fox and Kamprath (1970), over a 7-day period to confirm the length of time necessary to achieve equilibrium (Figure 1.13). This isotherm was prepared using a 200 mg L⁻¹ As spiking solution and 1:10 soil:solution ratio run at 25°C. Arsenic adsorption was rapid, with 90% of dissolved As(V) adsorbed after 60 min and >99% at 7 d. This finding is consistent with the rate of P sorption observed in various soils (Fox and Kamprath, 1970). The initial 60 min adsorption of As(V) on study soils is consistent with the findings of Goh and Lim (2004) in studies of As(V) adsorption on tropical soils with significant Fe oxyhydroxide content. They found that adsorption was best described by the Elovich kinetic model where the rate of As adsorption decreased exponentially over time with increasing As coverage on the soil surface. A reaction following the Elovich model provides a straight line when plotting sorbed concentration versus natural log time. Figure 1.13 clearly demonstrates the conformance with an Elovich model during the first 60 min, followed by slower adsorption (or potentially a precipitation mechanism) in the days following.

Upon confirmation that equilibrium was achieved over a 7-day adsorption period, equilibrium isotherms were developed for Typic Hydrudands (Olaa Series) and Acrudoxic Hydrudands (Ohia Series), using As(V) spikes in 10^{0.5} concentration increments from 10-1000 mg L⁻¹. The isotherms demonstrate the high As adsorption capacity of the study soils (Figure 1.14). At the highest As spike concentration (1000 mg L⁻¹), the Olaa soil sorbed 98% of available As, whereas the Ohia soil adsorbed >99%. The higher As adsorption capacity of the Acrudoxic Hydrudands soil is believed to be the result of higher reactive Fe content, the dominant As solid-phase sorbent in these soils. Because of the limited number of soils evaluated in this study for As adsorption capacity (N=2), a quantitative relationship between sorption capacity and soil mineralogy has not been established.

The adsorption capacity of As(V) on Hydrudands, relative to other soil types, is high (N. Hue, pers. comm.). The high As sorption capacity of volcanic-ash derived Hydrudands has resulted in elevated As levels in soils wherever arsenical herbicides were applied.

Andisols, with their unique mineralogy composed of short-range order iron oxyhydroxides and allophane-like aluminosilicates, strongly bind As and phosphate. At a soil pH of approximately 6, as observed in study soils, inorganic arsenate is near its adsorption maxima on amorphous Fe and Al oxides and common clay mineral sorbents (Goldberg, 2002).

Arsenic distribution in surface soils

Surface soil samples (N=90 sample locations) were collected across the study area from Hilo to Pahoia, within and adjacent to known cane cultivation areas. Total As was analyzed in the <2 mm soil fraction of air-dried samples by Bruker Tracer III-V portable EDXRF instrument using 300 s acquisition time. Replicate (N=8) analyses of a reference sample containing approximately 200 mg kg⁻¹ As showed an analytical measurement error (1 standard deviation, stdev) of 4 mg kg⁻¹, corresponding to a relative error (coefficient of variation, CV) of 2 percent. Naturally-occurring background levels of A_{STOT} in soils never cultivated for sugar cane are below 20 mg kg⁻¹ (USDA-NRCS, 2011). Within former cane cultivation areas (N=67 sample locations), where arsenical herbicides were applied, soil A_{STOT} concentrations were observed to range from 40 to 670 mg kg⁻¹, with an average of 260 ± 150 mg kg⁻¹ (mean ± 1 stdev) (Table 1.4).

Soil A_{STOT} concentrations are similar among the major cultivation areas. Soil from the former Ola'a Sugar Plantation (N=41), and the isolated plantings around the town of Pahoia (N=6), exhibit similar mean A_{STOT} concentration of 260 ± 160 and 280 ± 190 mg kg⁻¹, respectively. For the Waiakea Mill Company plantation lands (N=20) in the vicinity of Hilo, the average A_{STOT} is lower at 200 ± 120 mg kg⁻¹ (Table 1.4); however the mean A_{STOT} content in the Ola'a and Waiakea plantation soils are not statistically different at the 95 percent confidence level (two-tailed t-test, p>0.05).

Detailed plantation boundaries for the Ola'a Sugar Plantation circa 1926 are available from historical maps (Cook, 1926). Comparison of soil As concentrations with cultivation boundaries clearly shows the relationship between cane cultivation (and arsenical herbicide application) and elevated soil As content (Figure 1.15). Throughout the study area, all areas known to have been in sugar cane cultivation have elevated soil As levels. Some locations near Hilo Harbor not believed to have been in cane also show elevated soil As, possibly due to localized weed control with arsenical herbicides around facilities and roadways.

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 As contamination in former sugar cane lands. Fine fraction (<0.25 mm) samples from discrete depth intervals were analyzed for pH, TOC, elemental composition, reactive Fe (Si, Al and P) and A_{STOT} and A_{SBAC} (Table 1.5).

The Typic Hydudands (Olaa Series) profile (Figure 1.16) consists of 80 cm of soil development above a 'a 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 Hydudands (Ohia Series) profile 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 Bw₁ horizons) was 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, between 5.7 and 6.2 ± 0.1 (Figures 1.17 and 1.18). Total organic carbon content (TOC) ranges from 2.3 to 8.6 ± 0.05 wt % in the more weathered Ohia soils and 9.4 to 12.3 ± 0.05 wt% in the Olaa soil; in each profile, TOC is highest in the uppermost Ap horizon (plow zone).

Total As 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 A_{TOT} along the depth profile are highly variable, with peaks at 30 and 60 cm depth, separated by lower concentrations at 40 and 50 cm depth. In the Ohia profile, A_{TOT} is much lower than in the Olaa profile, ranging from <10 to 110 mg kg⁻¹. Similar to Olaa profile, A_{TOT} is highly variable, with peaks at 10 and 30 cm. Arsenic contamination above 20 mg kg⁻¹ is localized in soils shallower than 50 cm.

Total P in the soil profiles ranges from approximately 1000 to 3000 mg kg⁻¹. Ka'u Basalt contains approximately 1000 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 1000 to 1500 mg P kg⁻¹ (USDA-NRCS, 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, pers. comm.). Total P in soil above 1500 mg kg⁻¹ is likely the result of P-based fertilizer addition. Citrate-dithionite-extractable P (P_{CD}) in soil profiles ranges from 300 to 1300 mg kg⁻¹. P_{CD} is believed to represent P in association with reactive Fe substrate, but could include residual fertilizer compounds and a small fraction of igneous apatite (Ruttenberg, 1992). Reactive P in soil is expected to behave similarly to inorganic As in soil partitioning and mobility.

Total Fe and Al are higher in the Ohia profile than the Olaa profile, due to relative enrichment in the ash-dominant profile as compared to a lithic profile. Reactive Fe pools (Fe_{H AH} and Fe_{CD}) are distinctly different in the two profiles. For the less weathered Olaa sequence, Fe_{H AH} constitutes 35-50% of Fe_{TOT}, attesting to the presence of significant ferrihydrite-like Fe substrate. Fe_{CD} in this profile ranges from 35 to 50% of Fe_{TOT}, demonstrating that less than half of the Fe is in the form of reactive Fe oxyhydroxides or oxides; the balance likely remains in primary silicate mineral phases or unweathered

volcanic glass. The ash-rich Ohia profile has a lower percentage of Fe in ferrihydrite-like form (Fe_{HAH}) ranging from 4 to 16% of Fe_{TOT} , and Fe_{CD} content ranging from 70 to 92% of Fe_{TOT} . The proportion of Fe pools attest to the advanced weathered nature of the Ohia soil profile, with relatively low amounts of HAH-extractable Fe and a relative absence of partially weathered lithics.

Arsenic and phosphorus (phosphate in soil, PO_4) appear to behave similarly in the two soil profiles. Phosphorus concentrations above background levels (1500 mg kg^{-1}) are believed to reflect the application of phosphate fertilizers to cane soils. Introduction of P is similar to that of As, applied at the soil surface and potentially mixed by tillage to a depth of 30 to 35 cm. Both the depth of penetration into the soil profile and location of concentration peaks are similar for As and P. In the Olaa profile, coincident As and P (P_{TOT} and P_{CD}) peaks are observed at 20-30 and 60 cm depth, and both As and P concentrations approach background levels at a depth of 80 cm (the contact w/ underlying weathered rock). In the Ohia profile, As_{TOT} and P (P_{TOT} and P_{CD}) show coincident peaks at 10 and 30 cm depth, and both As and P reach background levels between 40 and 50 cm depth. In both profiles, As and P peaks are in part coincident with relative peaks in reactive Fe (Fe_{HAH} and Fe_{CD}); increased As and P retention within these specific horizons may be indicative of relatively higher Fe oxyhydroxide content (a strong As and P sorbent) and lower lithic content (a low As and P sorbent).

Downward migration of As (and P) through the Hydrudands soil profiles may be mediated by several processes, including migration of dissolved As in the soil solution, migration of soil colloids with sorbed As, physical mixing by human cultivation (plowing), and bioturbation by plant roots and biota. Batch desorption studies were conducted to evaluate the degree of As solubility in DI water and a synthetic soil solution ($0.01M \text{ CaCl}_2$). Results indicated very limited solubility, with no As detected at a method detection limit of approximately $1 \mu\text{g L}^{-1}$. Sequential extraction with CaCl_2 and Mehlich III reagents showed As desorption at low concentrations (Hue and Cutler, 2007). During periods of high water saturation, reducing conditions may develop in the soil column, and dissolution of Fe oxyhydroxide phases may occur resulting in increased release of sorbed As to the soil solution. The degree to which redox fluctuations affect As 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. 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 author pointed out that lower metal transport potential occurred in colloids with high Fe and Al 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 a'ā lava. This location is currently vegetated with guinea grass and coconut palms. In the Ohia profile, where agricultural practices have continued since sugar ceased, evidence of intensive plant root bioturbation extended to a depth of about 55 cm. In both profiles, evidence of intense plant root bioturbation was present throughout the zone of elevated As contamination, and may be a factor in downward transport of soil As and development of the vertical distribution of As in the soil profiles.

In summary, downward migration of As in the soil profile of Hydrudands is likely controlled by multiple mechanisms, including physical mixing by human cultivation and bioturbation. Downward migration of dissolved As, or As sorbed on soil colloids, within infiltrating soil solution is also believed to be a contributing transport mechanism. For the soil profiles inspected in the former sugar cane lands of the study area, As migration did not extend below materials with strong As sorption capacity; therefore, the underlying groundwater resources do not appear to be at risk from As contained in overlying soils. This does not preclude the potential for As to affect groundwater in other site scenarios, especially where soils are thin, the groundwater is shallow, and a significant As source in soil is present (for example, an As release at a chemical storage or mixing facility).

Bioaccessible arsenic in surface soils and vertical profiles

Bioaccessible As was evaluated in surface soils (N=26 sample locations) using the SBRC-g method. Measurements of AS_{BAC} ranged from 1.6 mg kg⁻¹ to 76 mg kg⁻¹, whereas $AS_{BAC}\%$ ranged from 1.6 to 35% (Table 1.6 and Figure 1.19). 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 cane cultivation. Acrudoxic Hydrudands, with higher reactive Fe content and a lower percentage of lithics and organics, showed the lowest percent bioaccessibility, averaging $4 \pm 2\%$ for the 6 soils tested. Typic and Lithic Hydrudands, which display a range of soil properties between highly weathered Acrudoxic Hydrudands and incipient Udifolists, averaged $9.2 \pm 4.5\%$ As bioaccessibility. The single Udifolists evaluated for AS_{BAC} showed 35% bioaccessibility, by far the highest percent AS_{BAC} value observed in former sugar cane surface soil of the study area (Table 1.6). A cross-plot of AS_{TOT} versus AS_{BAC} (Figure 1.19) displays the high variability in the percentage of As bioaccessibility in surface soils of the study area, however the trend of decreasing As bioaccessibility with increased soil weathering (Udifolists > Typic & Lithic Hydrudands > Acrudoxic Hydrudands) is apparent. Comparison of As bioaccessibility with soil Ca/Ti ratio (weathering index) further supports the finding of lower bioaccessibility in more weathered Andisols (Figure

1.20). Study soils are limited to Andisols on the Island of Hawaii, and it is not currently known whether the degree of As bioaccessibility continues to decrease as Andisols further weather to other soil orders (i.e. Oxisols).

Bioaccessible As was determined for soils in the two vertical soil profiles (Table 1.5). For the Typic Hydrudands profile, $As_{BAC\%}$ was 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), $As_{BAC\%}$ averaged approximately 4% of As_{TOT} ; these Bw horizon soils contain a higher percentage of potential As sorbents (Fe_{TOT} , Fe_{CD} , Al_{TOT}). The weathered rock zone below 80 cm depths has low concentrations of As_{TOT} (8 to 32 $mg\ kg^{-1}$), and low $As_{BAC\%}$ that may be related to the low As_{TOT} loading (see Chapter 2). The Acrudoxic Hydrudands profile shows significantly lower $As_{BAC\%}$ than the less weathered Typic Hydrudands, averaging about 2% of As_{TOT} in the Ap and Bw horizons. In summary, analysis of vertical profiles for As_{BAC} confirms surface soil findings that more weathered Acrudoxic Hydrudands have a lower percentage of As_{BAC} than Typic and Lithic Hydrudands.

The specific soil properties controlling the degree of As bioaccessibility are more fully evaluated in Chapter 2 – Soil Properties and their Influence on Arsenic Bioaccessibility in Hawaiian Andisols.

1.4. Bioaccessible Arsenic and the Need for Mitigating Actions

Soil As 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=67) of the former Waiakea and Ola'a sugar plantations is approximately 260 $mg\ kg^{-1}$, ranging from 40 to 670 $mg\ kg^{-1}$ (stdev 150 $mg\ kg^{-1}$). Soils used for cane cultivation are Hydrudands, a great group of the Andisol soil order. Hydrudands are characterized by hydrated, short-range order Fe oxyhydroxides, aluminosilicates and Al-Fe-humus complexes, and have a strong propensity to adsorb oxyanions such as phosphate and inorganic As (arsenite/arsenate). As a result of historical application of sodium arsenite herbicide solutions, high levels of residual As are found in shallow soils. While the properties of Hydrudands have led to sequestration of As, and As 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 have led to high As sequestration also prevent As migration to the underlying groundwater aquifer and limit its bioaccessibility and potential for human health hazard from incidental soil ingestion.

The average As bioaccessibility in study area Typic and Lithic Hydrudands is approximately 9 ± 5 percent of As_{TOT} , and for the more weathered Acrudoxic Hydrudands is only 4 ± 5 percent of As_{TOT} . Bioaccessible As, expressed in concentration form, ranges 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, show lower percent AS_{BAC} than Hydrudands with a substantial lithic content. Incipient organic soils, the Udifolists, show higher percent AS_{BAC} , although they were rarely used for sugar cane cultivation due to their shallow nature.

One Typic Hydrudands from the study area has been tested for both *in vivo* relative bioavailability in the cynomolgus monkey model (Roberts, 2007) and *in vitro* bioaccessibility by the SBRC method (Exponent, 2005; Lowney et al., 2007). Measured relative As bioavailability ($5 \pm 2\%$) and bioaccessibility (6.5%, no error provided) are similar, suggesting the SBRC-g test may be a valid surrogate for the costly *in vivo* test. Additional *in vivo* bioavailability work on As-contaminated soils is recommended to evaluate the appropriateness of *in vitro* methods and to better gauge the potential for human health risks from soil As exposure.

The HDOH (2006, 2010) has published recent guidance on management of As-contaminated soil, using AS_{BAC} to assess potential human health direct-contact hazard and the need for remedial actions. An average AS_{BAC} concentration of 23 mg kg^{-1} is proposed by HDOH (2010) as an action level, corresponding to a non-cancer hazard quotient of 1.0 and an excess lifetime cancer risk of $5E^{-5}$ under a residential exposure scenario (HDOH, 2006). Parcels with soils containing $AS_{BAC} < 23 \text{ mg kg}^{-1}$ (on average) are deemed “minimally impacted”, and do not require specific land use controls or remedial action. Soils with $AS_{BAC} > 23 \text{ mg kg}^{-1}$ typically require remediation, engineering controls or restricted land use (for example commercial or industrial). Based on the findings of this study, some soils within former sugar cane plantations are likely to have AS_{BAC} levels $< 23 \text{ mg kg}^{-1}$, and will not require action under HDOH guidance. However, it is likely that for some parcels of land, AS_{BAC} will exceed 23 mg kg^{-1} (on average), and will trigger the need for some form of mitigation.

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Table 1.1 Soil Analysis Methods

Soil Property	Soil Fraction	Soil Preparation	Analytical Method
Elemental Composition	<2 mm	Fused glass disks	WDXRF
" "	<2 mm, <0.25 mm	Air and oven dried	EDXRF, acid digestion/ICPOES
" "	<0.25 mm	Air dried	Electron microprobe spectroscopy
Mineralogy	<2 mm	Air dried	Petrographic microscopy
" "	<10 µm	Wet sieved, moist	TEM
Loss on ignition	<0.25 mm	Air dried	Furnace @ 750°C
Arsenic Speciation	<2 mm	Field moist, N ₂ atmosphere	XAS
Sorption Isotherms	<2 mm	Air dried	Batch sorption tests/ICPMS
Bioaccessible Arsenic	<0.25 mm	Air dried	In vitro extraction/ICPMS
Reactive Fe, Al, Si	<0.25 mm	Air dried, ground	Targeted chemical extractions/ICPOES

WDXRF - Wavelength dispersive X-ray fluorescence

EDXRF - Energy dispersive X-ray fluorescence

ICPOES - Inductively coupled plasma optical emission spectrometry

ICPMS - Inductively coupled plasma mass spectrometry

TEM - Transmission electron microscopy

XAS - X-ray absorption spectroscopy

Targeted chemical extraction included citrate-dithionite and hydroxylamine hydrochloride

Table 1.2 Comparison of In Vitro Assay Methods^a, OIaa Series Hydrudands

Sample	As_{TOT}^b	$PBET^c$		IVG^d		$SBRC^e$	
	$mg\ kg^{-1}$	$As_{BAC\%}$		$As_{BAC\%}$		$As_{BAC\%}$	
		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
Std. Dev.	88	0.8	0.9	1.2	1.2	1.7	0.4

Samples are Ap horizon soils from locations in vicinity of Keaau, Hawaii

^a Data provided by HDOH (2007), laboratory analysis by M. Lord-Hoyle, Royal Military

College of Canada under contract to HDOH

^b Total As by HCl and HNO₃ digestion, ICP

^c after method of Ruby et al. (1996)

^d after method of Rodriguez et al. (1999)

^e after method of Kelley et al. (2002), Drexler and Brattin (2007)

Table 1.3 Major element composition of Kau Basalt and associated soils

Matrix	Name	Age Underlying Lava	N ^b	Si	Ti	Al	Concentration (wt. %) - in mineral solids ^a						
							Fe	Mn	Mg	Ca	Na	K	P
rock	Kau Basalt ^c		63	23.4 ± 0.7	1.1 ± 0.2	6.6 ± 1.0	8.7 ± 0.3	0.13 ± 0.01	7 ± 3	6.7 ± 0.9	1.5 ± 0.3	0.27 ± 0.10	0.10 ± 0.02
soil ^d	Udifolists	<1500 Y	5	23.5 ± 0.6	1.49 ± 0.11	7.5 ± 0.7	9.4 ± 0.6	0.15 ± 0.01	4.7 ± 0.6	7.0 ± 0.6	0.95 ± 0.19	0.38 ± 0.03	0.28 ± 0.11
soil ^d	Typic and Lithic Hydrudands	1,500-10,000 Y	23	19.3 ± 1.5	1.6 ± 0.3	8.7 ± 1.5	13.0 ± 1.6	0.18 ± 0.02	9 ± 2	4.0 ± 0.8	0.35 ± 0.16	0.20 ± 0.05	0.36 ± 0.17
soil ^d	Acrodoxic Hydrudands	10,000-30,000 Y	4	11.0 ± 1.8	3.5 ± 0.4	17.0 ± 1.4	22 ± 2	0.28 ± 0.01	2.3 ± 0.9	1.4 ± 0.7	0.08 ± 0.13	0.22 ± 0.02	0.63 ± 0.18

QA/QC Data - Evaluation of Analytical Variance

Matrix	Sample ID	# Reps ^e	Si	Ti	Al	Fe	Mn	Mg	Ca	Na	K	P	
soil ^d	SHP-01	3	0.11	0.02	0.4	0.08	0.01	0.3	0.08	0.04	0.01	0.02	
	SHP-02	4	0.19	0.05	0.4	0.09	0.01	0.3	0.10	0.04	0.02	0.03	
	SHP-07	4	0.08	0.05	0.4	0.03	0.01	0.5	0.09	0.02	0.02	0.02	
	SHP-11	4	0.13	0.08	0.6	0.05	0.01	0.3	0.13	0.05	0.03	0.02	
	SHP-13	3	0.06	0.01	0.02	0.01	0.01	0.01	0.04	0.02	0.01	0.01	
	SHP-22	4	0.17	0.07	0.6	0.10	0.01	0.3	0.02	0.04	0.02	0.03	
	SHP-33	3	0.02	0.01	0.03	0.02	0.01	0.06	0.01	0.01	0.01	0.01	
		Average Stdev ^f		0.11	0.04	0.3	0.05	0.01	0.3	0.07	0.03	0.02	0.02
		Ave Coefficient of Variation		0.5%	3%	4%	0.5%	3%	4%	1.3%	5%	6%	6%

^a Element concentrations for soils by WDXRF reported (mean ± 1 stdev) in dry weight basis after furnace combustion at 750°C

^b Number of rock or soil samples

^c Kau Basalt chemistry from Wolfe and Morris (1996)

^d < 2 mm soil fraction

^e Number of replicate analyses for subject sample

Table 1.4 Total arsenic in surface soils of former sugar cane planting areas

Plantation	N	As _{TOT} (mg kg ⁻¹) ^{a,b}		
		Min	Max	Mean ± 1 stdev
Olaa Sugar Company	41	50	670	260 ± 160
Olaa Pahoia Plantings	6	74	490	280 ± 190
Waiakea Mill Company	20	40	480	200 ± 120
Olaa and Waiakea combined	67	40	670	260 ± 150

^a < 2 mm soil fraction, air dried, analyzed by EDXRF

^b Replicate analyses indicate error (coefficient of variation) of 4%

Table 1.5 Vertical soil profile data^a

Depth (cm)	Horizon ^b	pH ^c	TOC ^d (wt. %)	Fe _{TOT} ^e (wt. %)	Fe _{HAH} ^f (wt. %)	Fe _{CD} ^g (wt. %)	Al _{TOT} ^h (wt. %)	Si _{TOT} ⁱ (wt. %)	P _{TOT} ^j (mg kg ⁻¹)	P _{DITH} ^k (mg kg ⁻¹)	As _{TOT} ^l (mg kg ⁻¹)	As _{BAC} ^m (mg kg ⁻¹)	As _{BAC%} ⁿ (%)
Typic Hydrudands profile													
10	Ap	5.7	12.3	8.62	1.14	3.09	5.81	13.18	2340	640	330	28	8.6%
20	Ap	5.9	9.5	9.63	1.19	3.76	6.93	14.18	2930	740	400	29	7.2%
30	Bw	5.9	9.7	10.31	1.49	4.94	7.03	13.51	2470	580	660	24	3.7%
40	Bw	6.0	7.2	10.94	1.39	4.50	7.41	13.67	1700	360	330	14	4.3%
50	Bw	6.1	7.0	11.16	0.99	4.60	8.04	13.45	2010	410	180	7.7	4.3%
60	Bw	6.0	9.4	10.76	1.47	5.34	6.98	11.98	2420	740	440	18	4.1%
80	Bw/C	5.9	8.2	9.41	0.91	3.34	8.45	12.48	1390	250	95	5.6	5.9%
100	C	5.8	5.5	6.77	0.50	1.72	9.60	14.31	1600	190	32	1.0	3.1%
120	C	5.9	4.0	6.01	0.33	0.92	9.01	14.84	1120	60	21	0.6	2.8%
140	C	5.9	4.3	5.74	0.45	0.96	10.94	14.33	1660	ND	7.9	<1	--
Acrudoxic Hydrudands profile													
10	Ap	5.9	8.61	14.03	2.04	10.74	10.51	8.04	3140	1150	99	1.6	1.6%
20	Ap	5.8	7.9	14.61	1.55	11.34	10.80	8.67	2670	1120	36	0.7	1.9%
30	Ap	5.9	8.2	14.60	2.39	10.73	10.63	8.29	3040	1270	110	2.3	2.1%
40	Bw1	6.0	5.1	14.65	1.31	10.27	13.09	6.25	2030	710	49	1.0	2.1%
50	Bw1	6.0	3.2	14.00	0.50	10.78	13.85	6.04	1250	480	13	<1	--
60	Bw2	6.1	2.7	17.28	0.90	13.37	15.59	3.53	1190	350	8.6	<1	--
70	Bw2	6.1	2.3	18.76	0.86	15.94	15.27	3.27	1120	290	16	<1	--
80	Bw2	6.2	2.5	17.49	0.81	13.68	14.42	3.94	1110	300	16	<1	--
90	Bw2	6.2	2.5	13.39	0.73	12.35	10.25	4.35	1090	340	9.0	<1	--

^a < 0.25 mm soil fraction

^b Ap = A horizon, plowed; Bw = B horizon, weathered, C = weather rock

Subscripts: TOT=total, HAH=hydroxylamine hydrochloride extractable, DITH=citrate-dithionite extractable, BAC=bioaccessible (SBRC-g meth

^c Stdev 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_{DITH} 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_{BAC} by SBRC-g. Replicate measurements of NIST 2710 control soil indicate CV of 9%.

Table 1.6 Total and bioaccessible arsenic in surface soils^a

ID	Soil Type ^b	As _{TOT} ^c (mg kg ⁻¹)	As _{BAC} ^d (mg kg ⁻¹)	As _{BAC} (%)	
HLO-08	Acrudoxic Hydrudands	210	3.7	1.8%	
KIP-10	Acrudoxic Hydrudands	99	1.6	1.6%	
SHP-14	Acrudoxic Hydrudands	130	5.2	4.0%	
SHP-49	Acrudoxic Hydrudands	340	18	5.2%	
SHP-51	Acrudoxic Hydrudands	240	8.8	3.7%	
SHP-53	Acrudoxic Hydrudands	44	3.6	8.1%	
HLO-05	Lithic Hydrudands	150	11	7.4%	
HLO-11	Lithic Hydrudands	390	13	3.3%	
HLO-12	Lithic Hydrudands	190	5.6	2.9%	
SHP-23	Lithic Hydrudands	120	18	15%	
SHP-26	Lithic Hydrudands	340	26	7.6%	
SHP-40	Lithic Hydrudands	65	7.4	11%	
HLO-02	Typic Hydrudands	110	7.8	7.1%	
KMS-5	Typic Hydrudands	380	30	7.9%	
SHP-03	Typic Hydrudands	340	76	22%	
SHP-07	Typic Hydrudands	290	26	9.0%	
SHP-08	Typic Hydrudands	380	53	14%	
SHP-10	Typic Hydrudands	150	19	13%	
SHP-17A	Typic Hydrudands	190	17	8.9%	
SHP-24	Typic Hydrudands	270	28	11%	
SHP-27	Typic Hydrudands	120	11	8.9%	
SHP-30	Typic Hydrudands	260	13	4.9%	
SHP-34	Typic Hydrudands	230	20	8.6%	
SHP-43	Typic Hydrudands	410	23	5.6%	
STS-010	Typic Hydrudands	400	29	7.2%	
SHP-36	Typic Udifolists	160	56	35%	
	N	26	26	26	
	Min	44	1.6	1.6%	
	Max	410	76	35%	
	Average	231	20	9%	
	Stdev	114	18	7%	
	Summary by Soil Type		n	Ave. As _{BAC} (%)	Stdev
	Acrudoxic Hydrudands		6	4%	2%
	Typic and Lithic Hydrudands		19	9%	5%
	Udifolists		1	35%	

^a < 0.25 mm soil fraction^b from USDA-NRCS (2010a)^c Analysis of As_{TOT} by acid digestion and ICPMS. Replicate measurements (N=4) of NIST 2710 control soil indicates error (coefficient of variance) of 6%.^d Analysis of As_{BAC} by SBRC-g. Replicate measurements (N=5) of NIST 2710 control soil indicates error (coefficient of variance) of 9%.

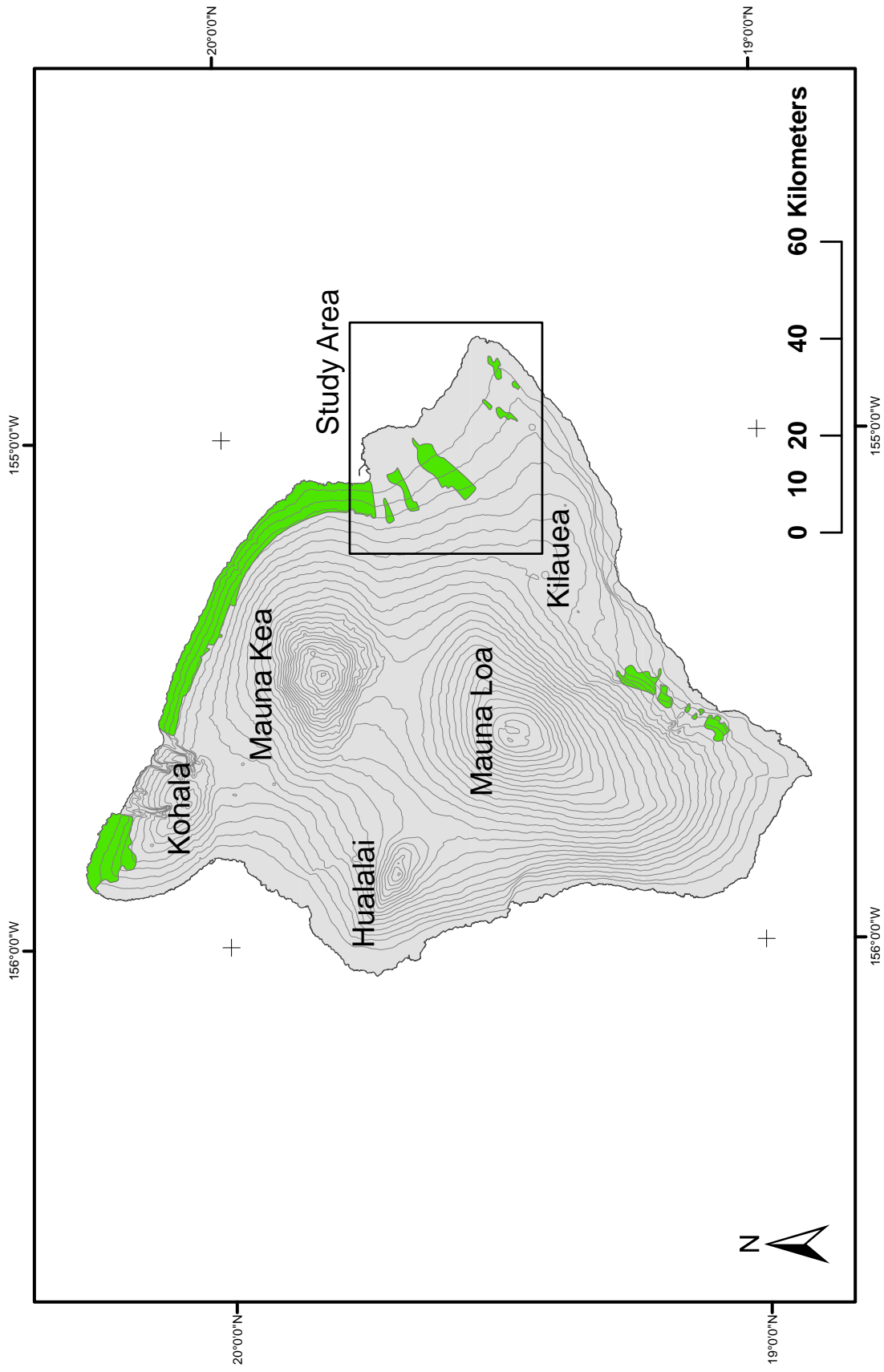


Figure 1.1 Location of sugar cane cultivation on Island of Hawaii, circa 1937 (Territory of Hawaii, 1937). Study area includes several discontinuous cane plantations south of Hilo on the east flank of Mauna Loa and Kilauea volcanoes.

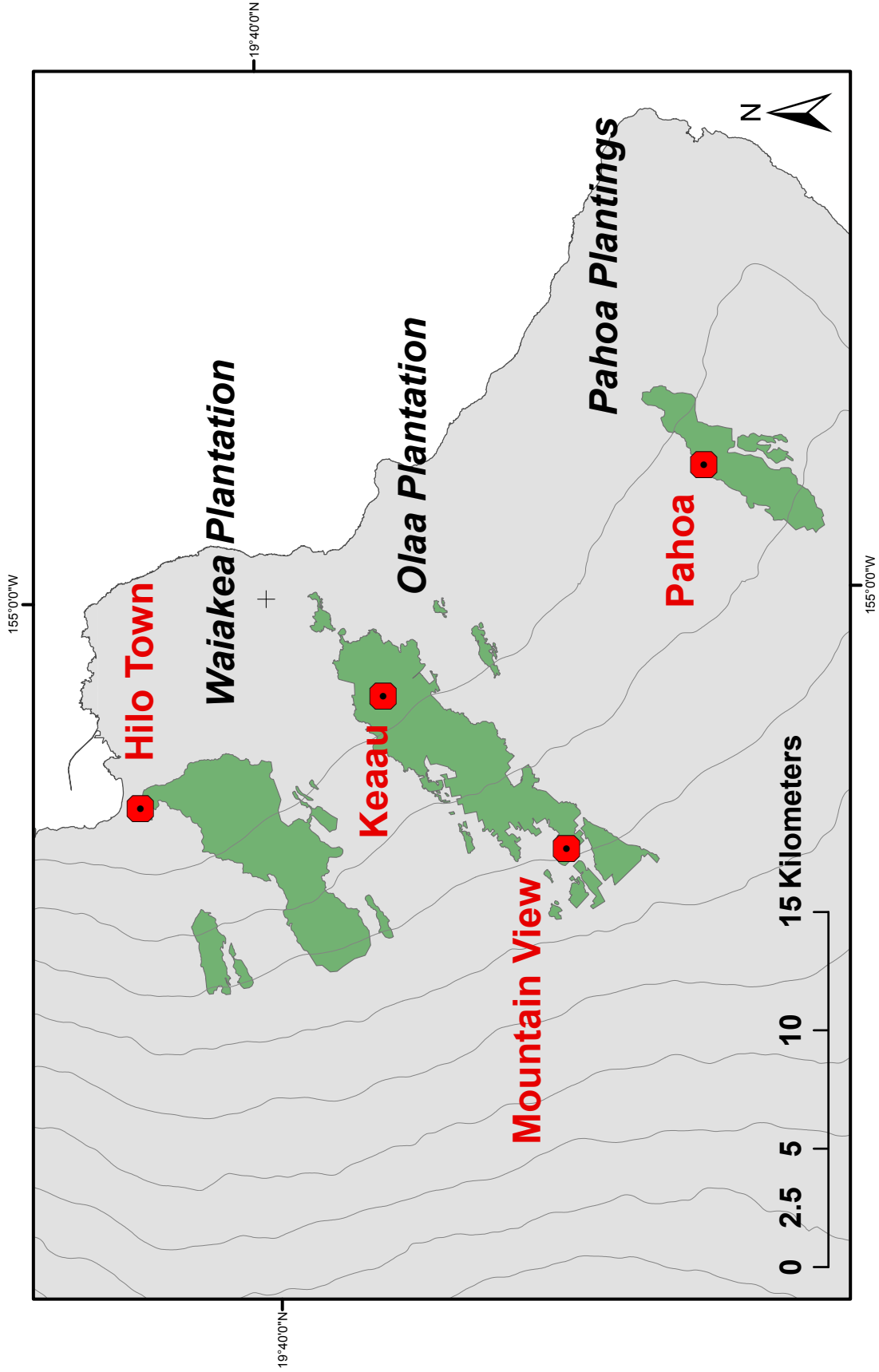


Figure 1.2 Current towns and former sugar cane plantations, eastern portion of the Island of Hawaii. Plantation extents derived from Cook (1920), Williams (1933) and Territory of Hawaii (1939).

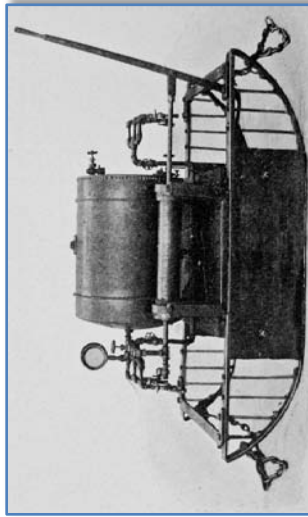
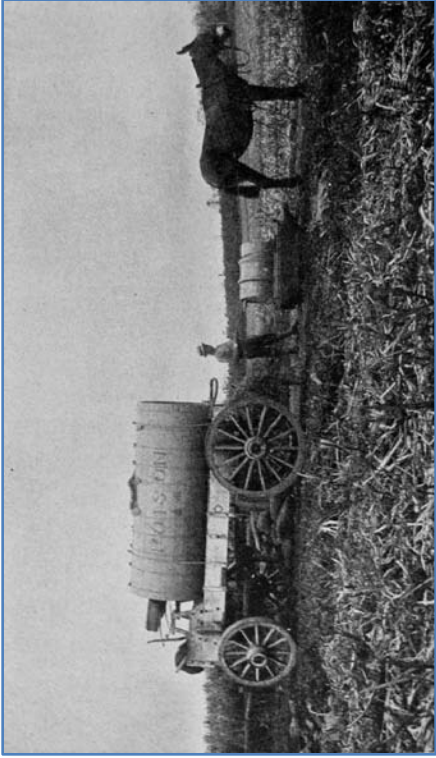


Figure 1.3 Arsenical herbicide application at Olaa Sugar Company plantation, 1914 (Larsen (1914a)). Clockwise from upper left: man with hand-pump knapsack sprayer, mule-drawn supply tank of arsenite of soda, gang of workers spraying weeds in young sugar cane, sled-based sprayer.

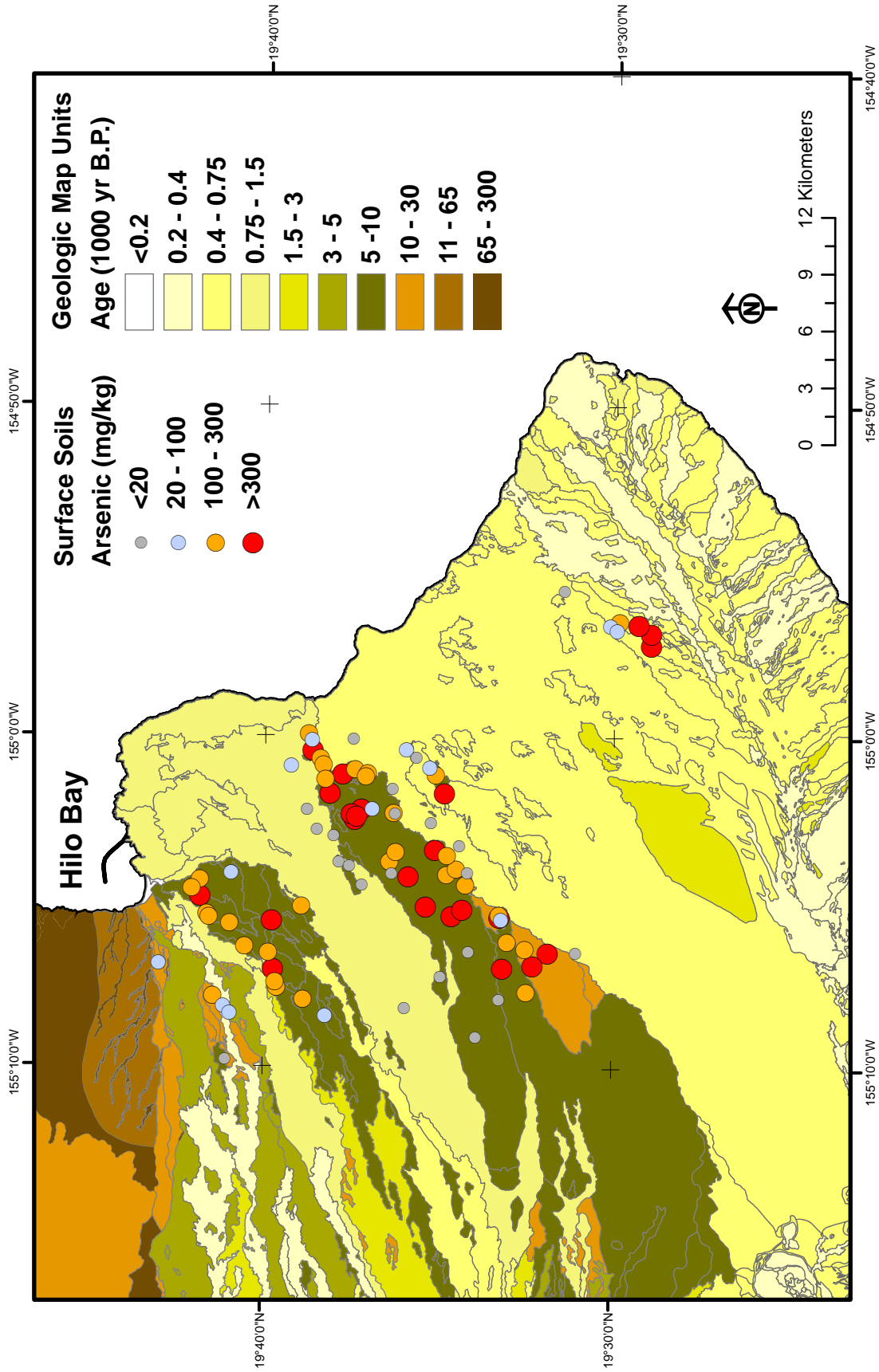


Figure 1.4 Geological map (Wolfe and Morris, 1996) with surface soil arsenic concentrations. Note most of cane plantings and higher soil arsenic concentrations are coincident with lava flows at least 3,000 yr old, in which 0.5 m or more of soil has developed.

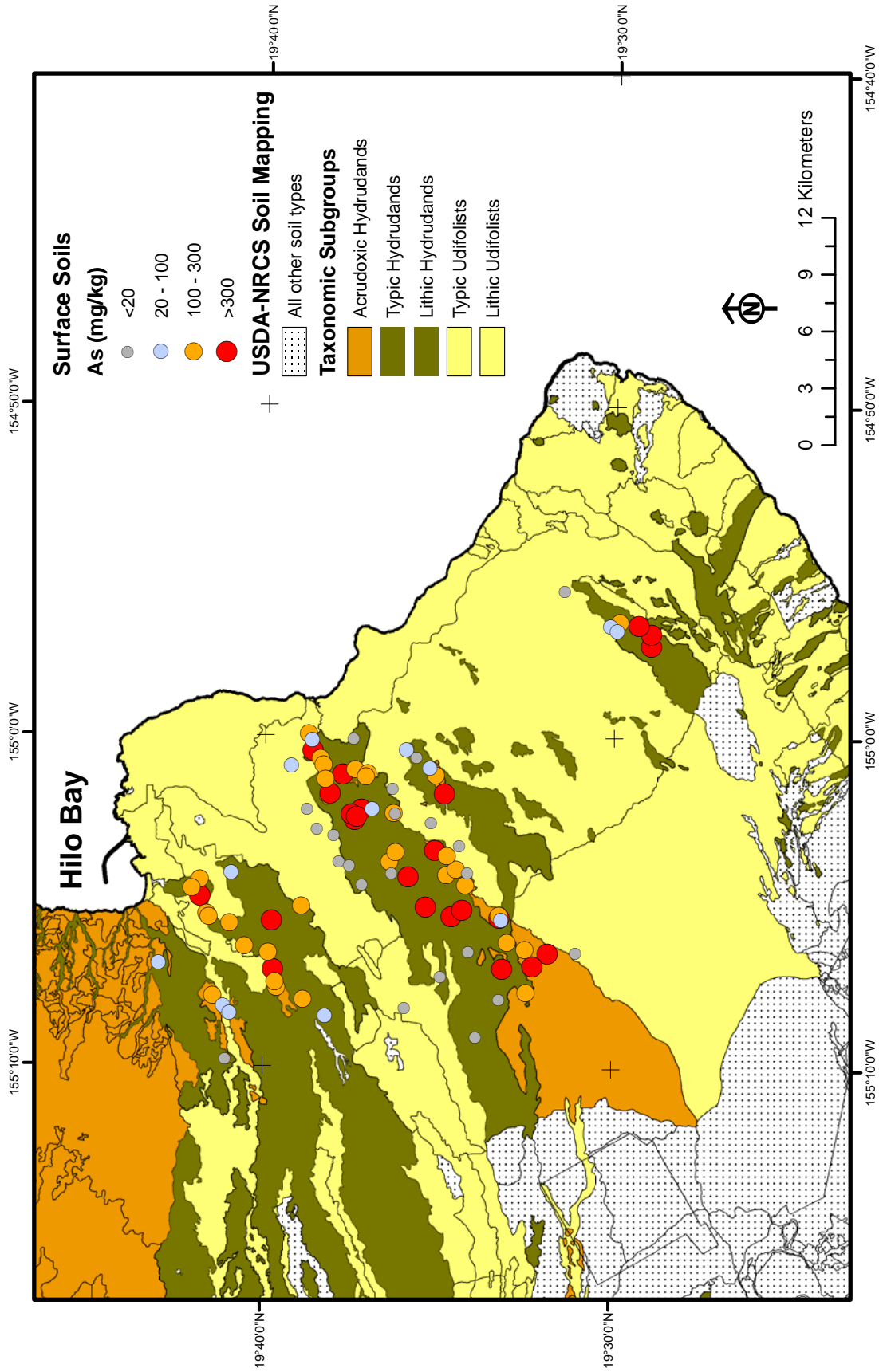


Figure 1.5 Soil survey map (USDA-NRCS, 2010a) with surface soil arsenic concentrations. Sugar cane plantings and elevated soil arsenic levels are coincident with development of Hydruandans soils; Udifolists are too thin to support cane.

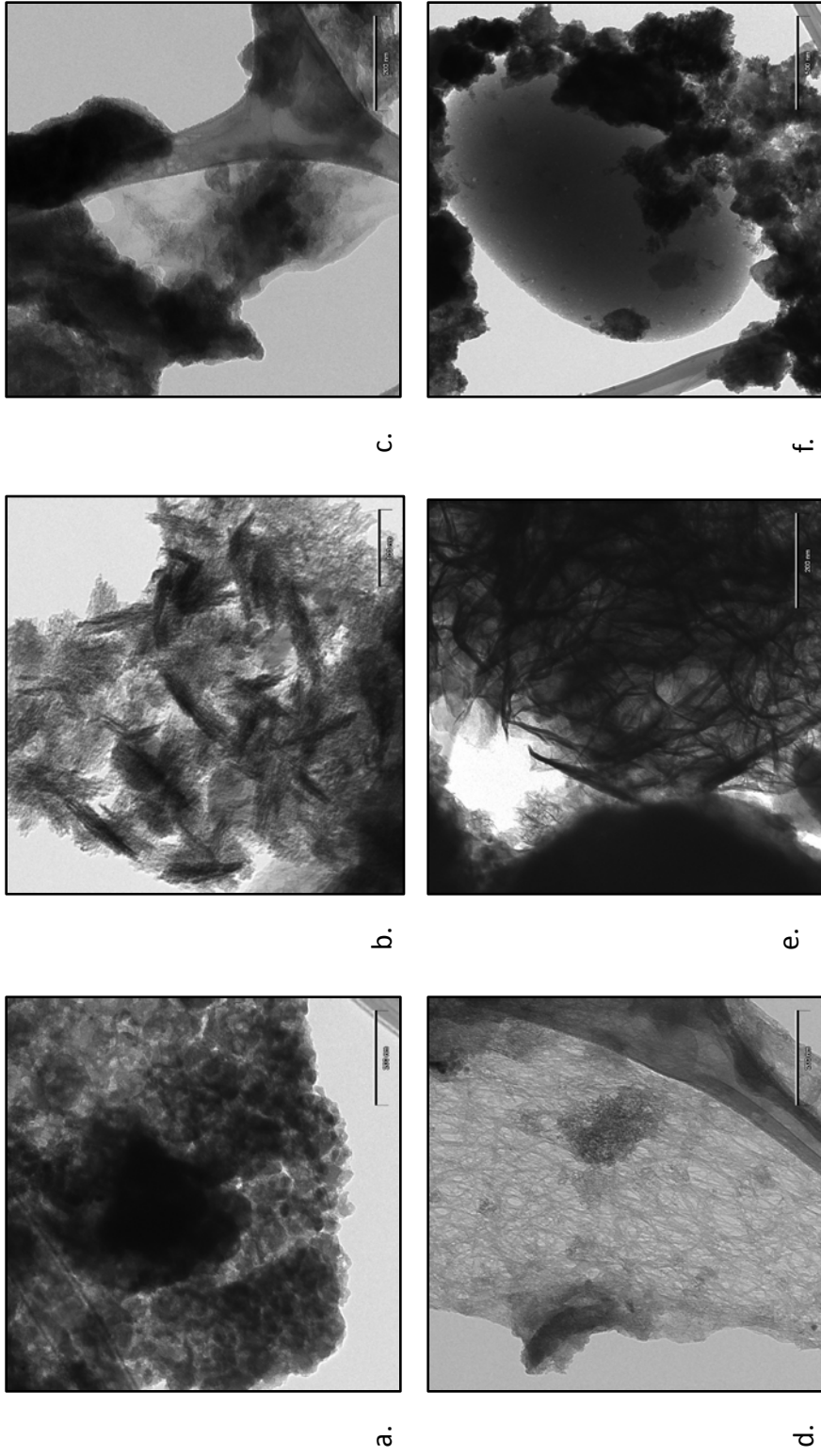


Figure 1.6 TEM photomicrographs, length of scale bars in parentheses: a.ferrihydrite-like Fe oxyhydroxide (200 nm), b.incipient goethite in ferrihydrite (100 nm), c. gel-like material clinging to sample frame (200 nm), d. imogolite (200 nm), e. smectite (200 nm), f. opaline silica surrounded by Fe oxyhydroxide aggregates (500 nm)

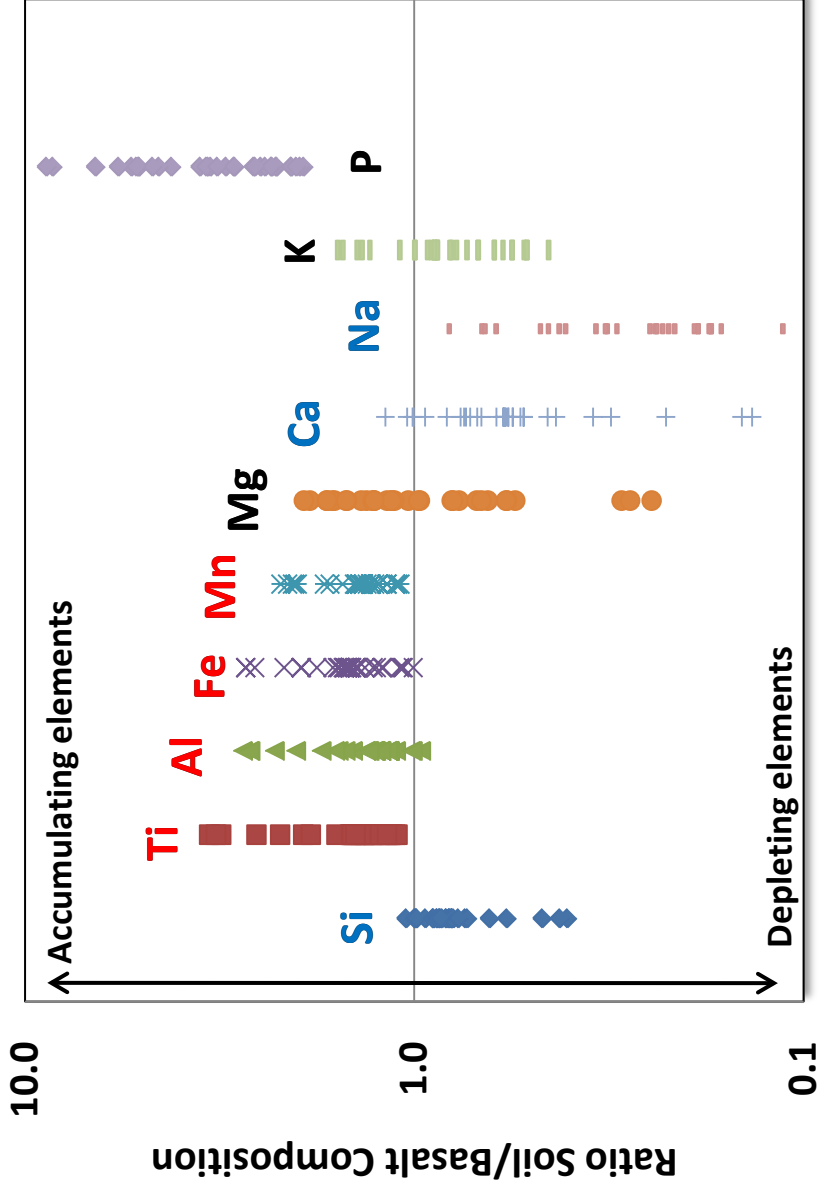


Figure 1.7 Major element compositions in study soils (<2 mm fraction), compared to mean Kau Basalt composition (Wolfe and Morris, 1996). Variable weathering leads to accumulation of Ti, Al, Fe, Mn and P, and depletion of Si, Ca, and Na. Element concentrations for soils expressed in dry weight basis after furnace combustion at 750 C, representative of mineral fraction less water and organic compounds.

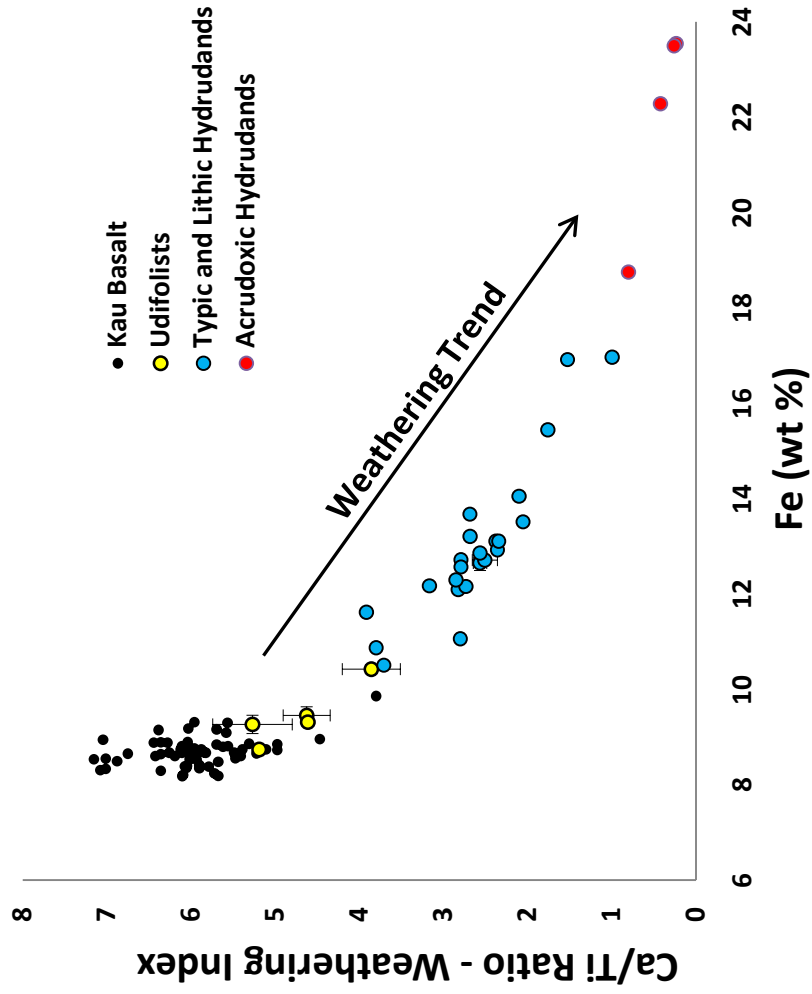


Figure 1.8 – Crossplot of Ca/Ti ratio versus total Fe for Kau Basalt (Wolfe and Morris, 1996) and associated soils (<2 mm fraction). Element concentrations for soils expressed in dry weight basis after furnace combustion at 750 C. Error bars are 2 stdev of mean for replicate analyses of study soils; Ca/Ti error bars reflect error propagated in fraction term. Trend of increasing Fe content and decreasing Ca/Ti ratio consistent with development of more weathered soil types.

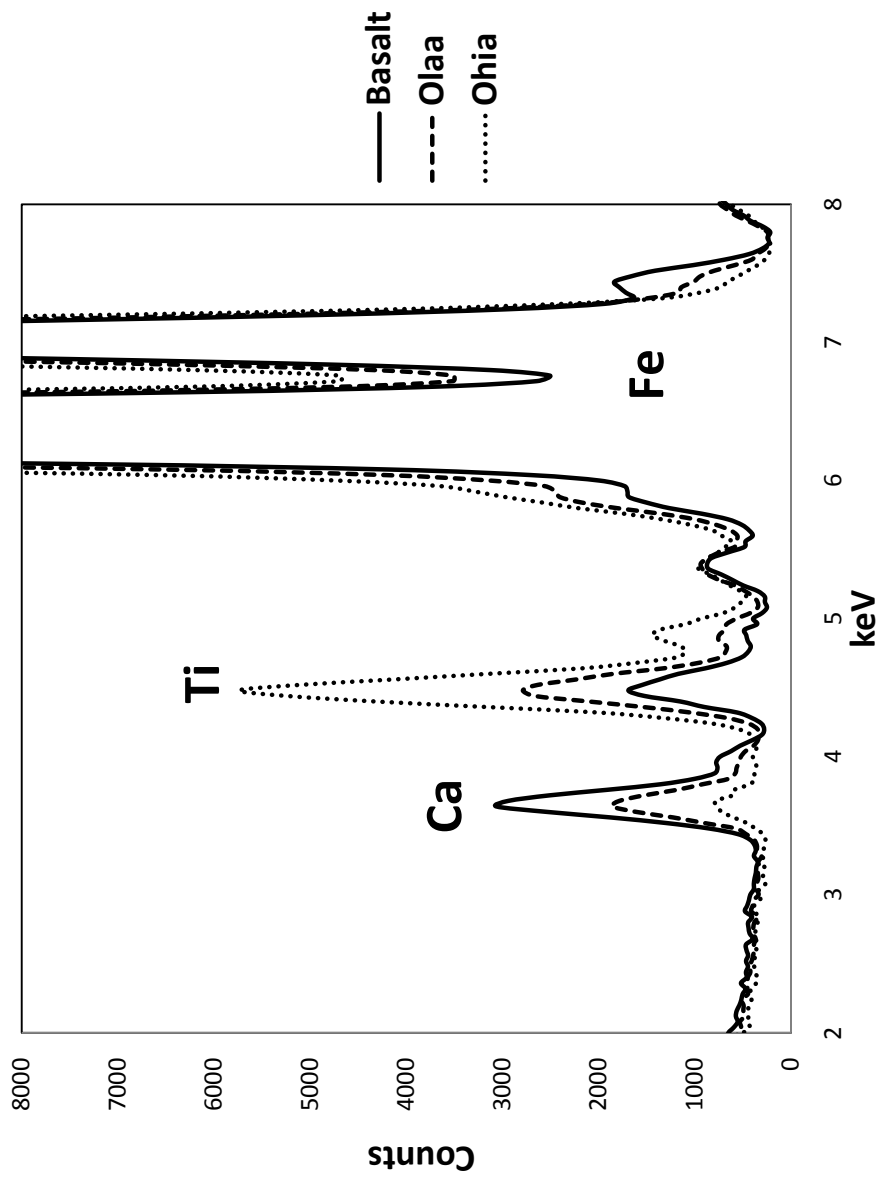


Figure 1.9 EDXRF spectra of a Kau Basalt, moderately weathered Lithic Hydrudands (Olaa Series) and highly weathered Acrudoxic Hydrudands (Ohia Series). Progressive loss of Ca and accumulation of Ti in soil weathering process is apparent from relative peak heights. Qualitative inspection of EDXRF spectra provides indication of degree of soil weathering.

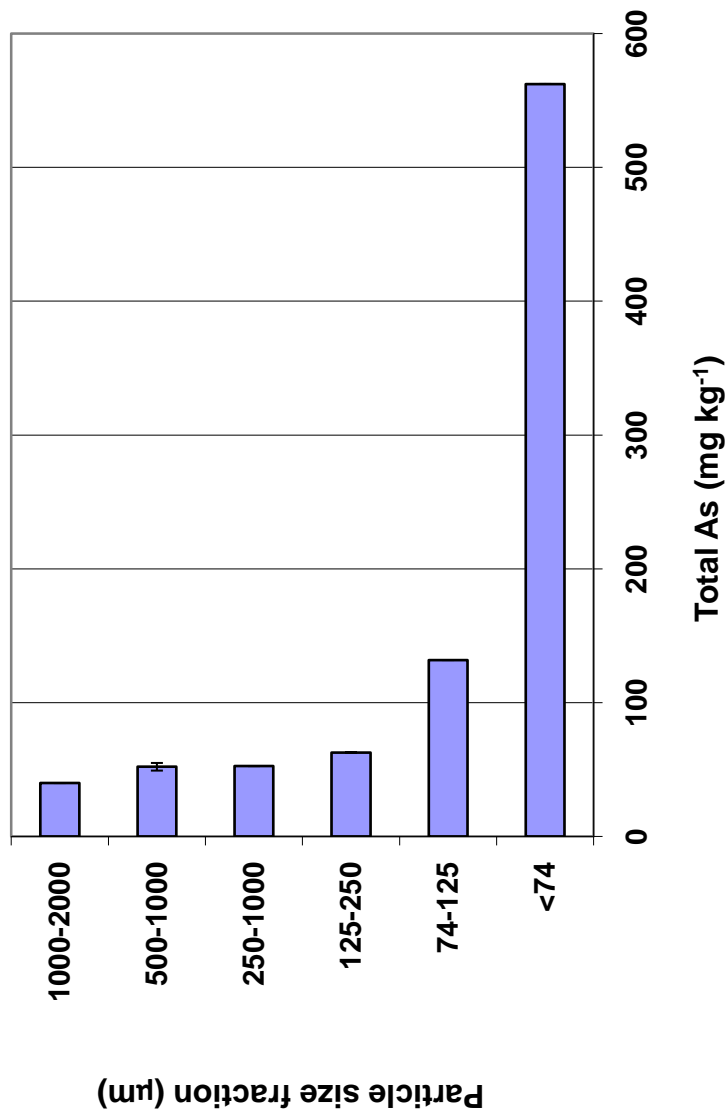


Figure 1.10 Total arsenic content in various grain size fraction of a Typic Hydrudands (Olaa Series). Particle size fraction prepared by wet sieve method. Duplicate analyses of 500-1000 µm fraction sample have 6 percent relative difference (error bar shows range of values). Arsenic is concentrated in the finer grain size fractions, which contain a higher percentage of secondary solid phases (Fe oxyhydroxides and poorly crystalline aluminosilicates) and lower percentage of unweathered volcanic lithics. The bulk soil (<2 mm) showed As concentration of 420 mg kg⁻¹.

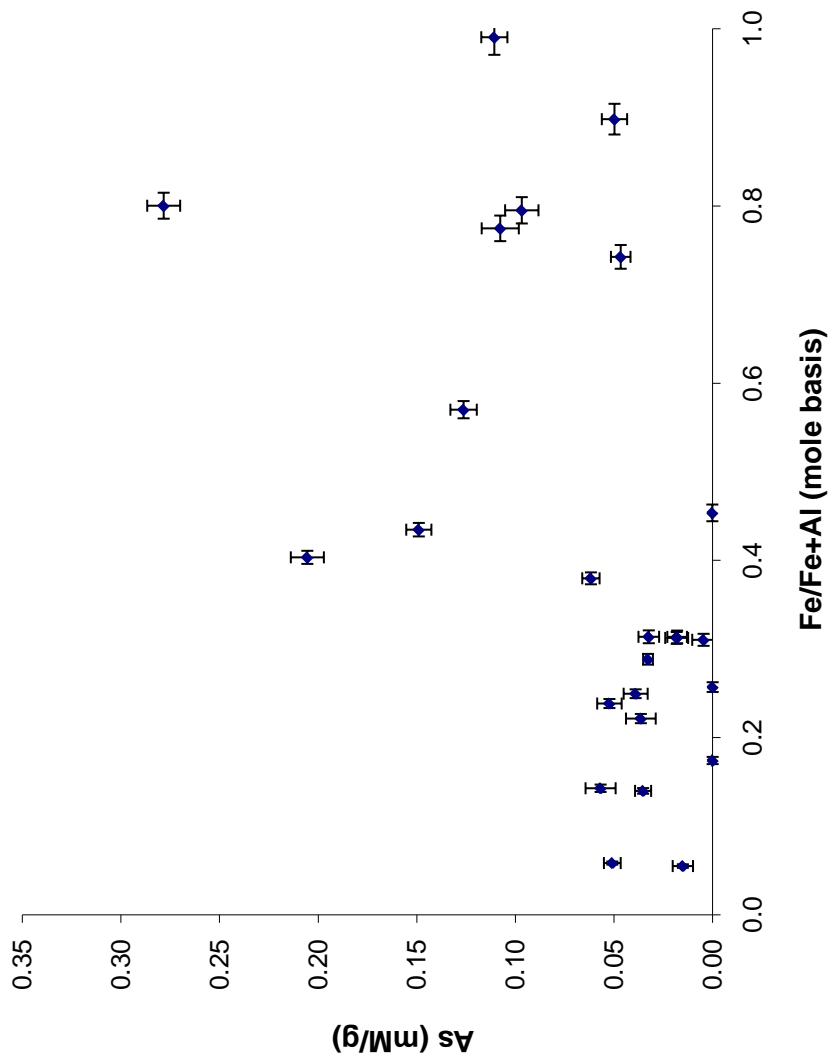


Figure 1.11 Microprobe elemental analysis of pedogenic solid phases in a Typic Hydrudands (Olaa Series). As content at various point locations in sample plotted against relative Fe versus Al content of substrate. As concentrations are generally higher in substrates dominated by Fe oxyhydroxides, with lower As content observed in substrates dominated by Al (aluminosilicates). Error bars show 95% confidence interval of analytical measurements, based on count statistics and concentration of standards. Data provided by Dr. John Drexler, University of Colorado, Boulder.

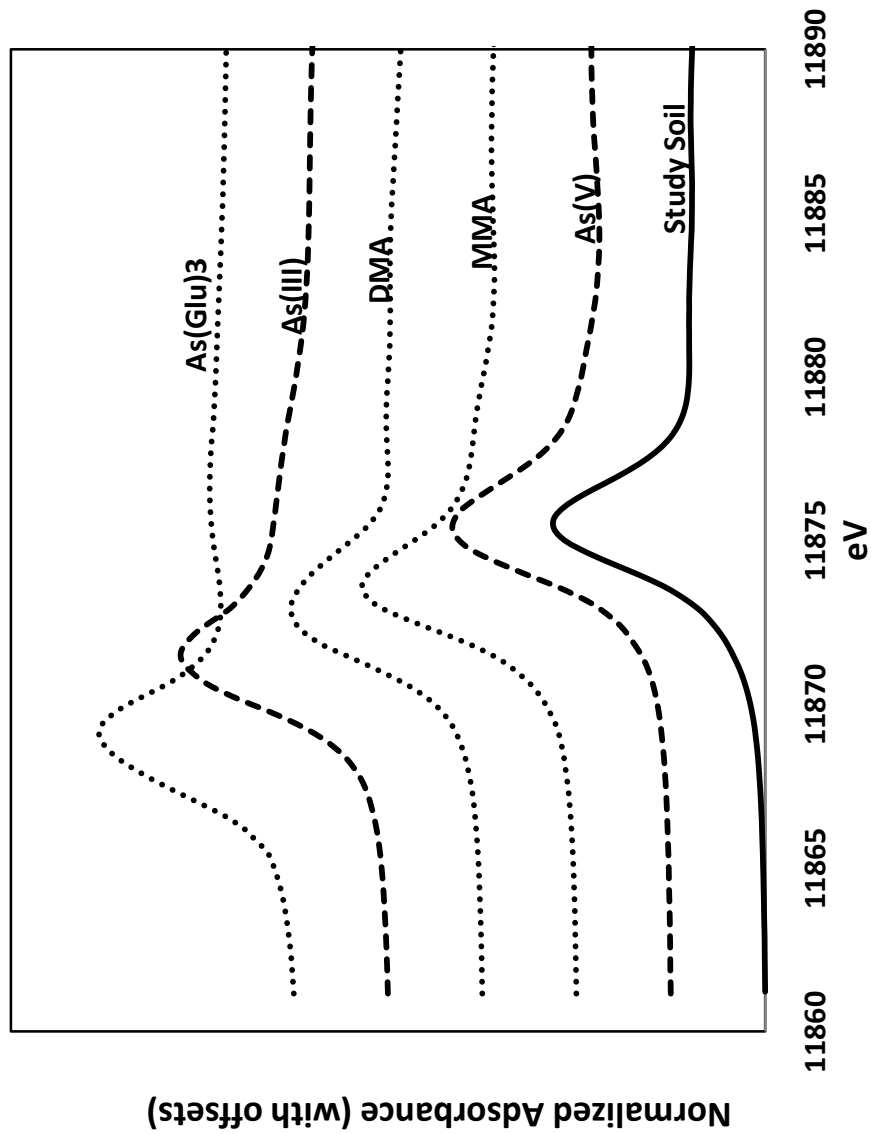


Figure 1.12 XANES spectra of Typic Hydridands (Olaa Series) soil, compared to various arsenic standards (from Meharg et al., 2008). Arsenic in subject soil is dominantly in the inorganic As(V) state.

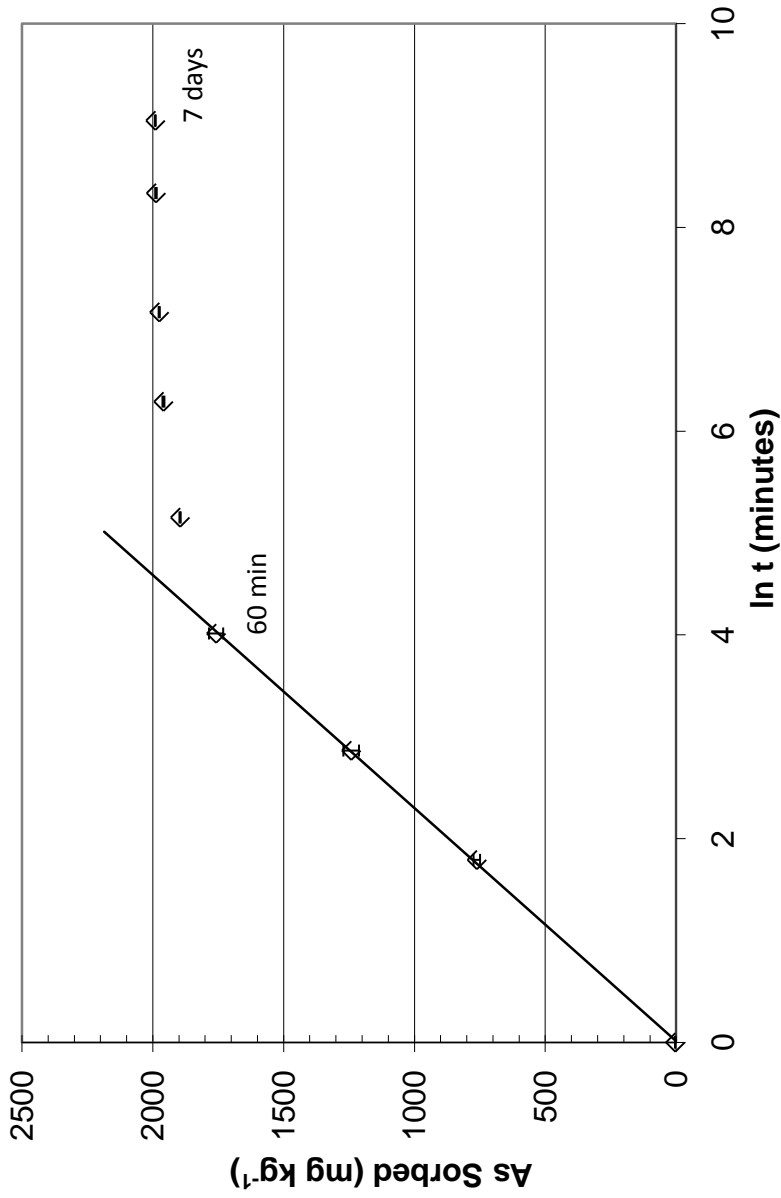


Figure 1.13 Arsenate kinetic sorption isotherm for a Typic Hydudands (Olaa Series, Ap horizon), <2 mm soil fraction. Sodium arsenate spike concentration 200 mg L⁻¹, 10:1 solution:soil ratio, 25 C. More than 90 percent As sorption after 1 hr, 99 percent As sorption after 7 d. Error bars show 2 stdev of triplicate tests for each time step.

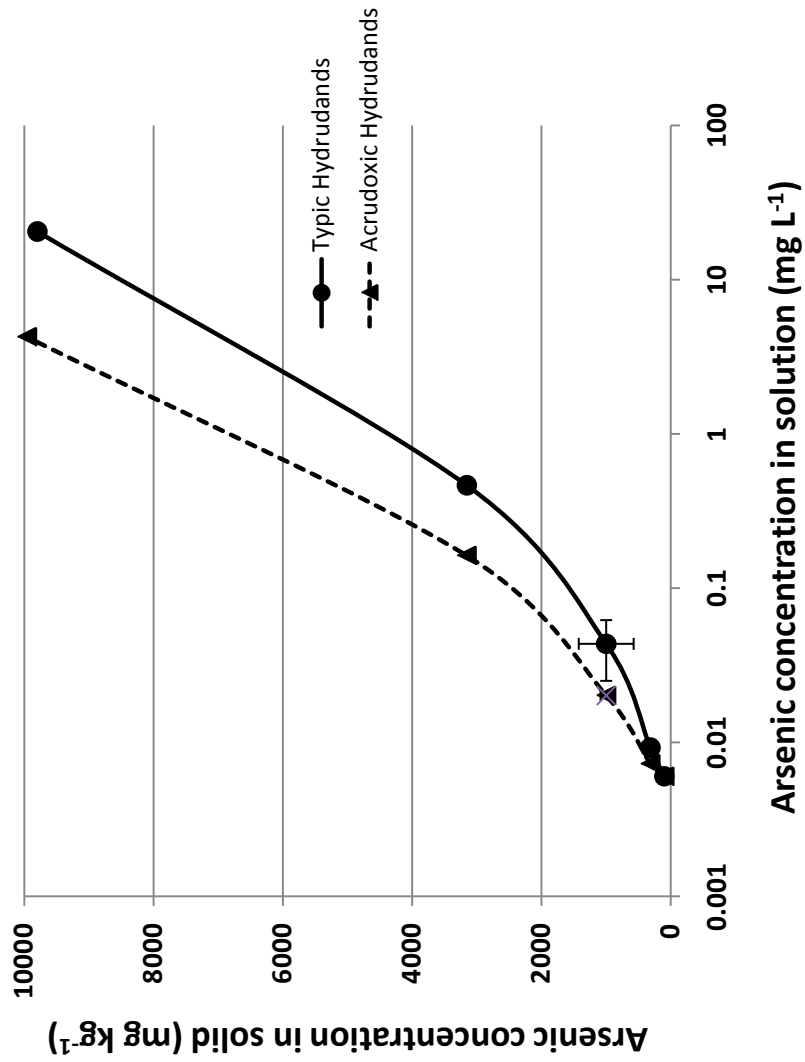


Figure 1.14 Arsenate equilibrium isotherms on < 2mm soil fraction of Typical Hydruandands (Olaa Series, Ap horizon) and Acrudoxic Hydruandands (Ohia Series, Ap horizon). Acrudoxic Hydruandands, with higher proportion of pedogenic Fe oxyhydroxides and aluminosilicates exhibit stronger As sorption capacity. Error bars indicate range of duplicate samples for sorption tests with 100 mg L⁻¹ spike; for Acrudoxic Hydruandands tests, error bars are smaller than symbol for average value.

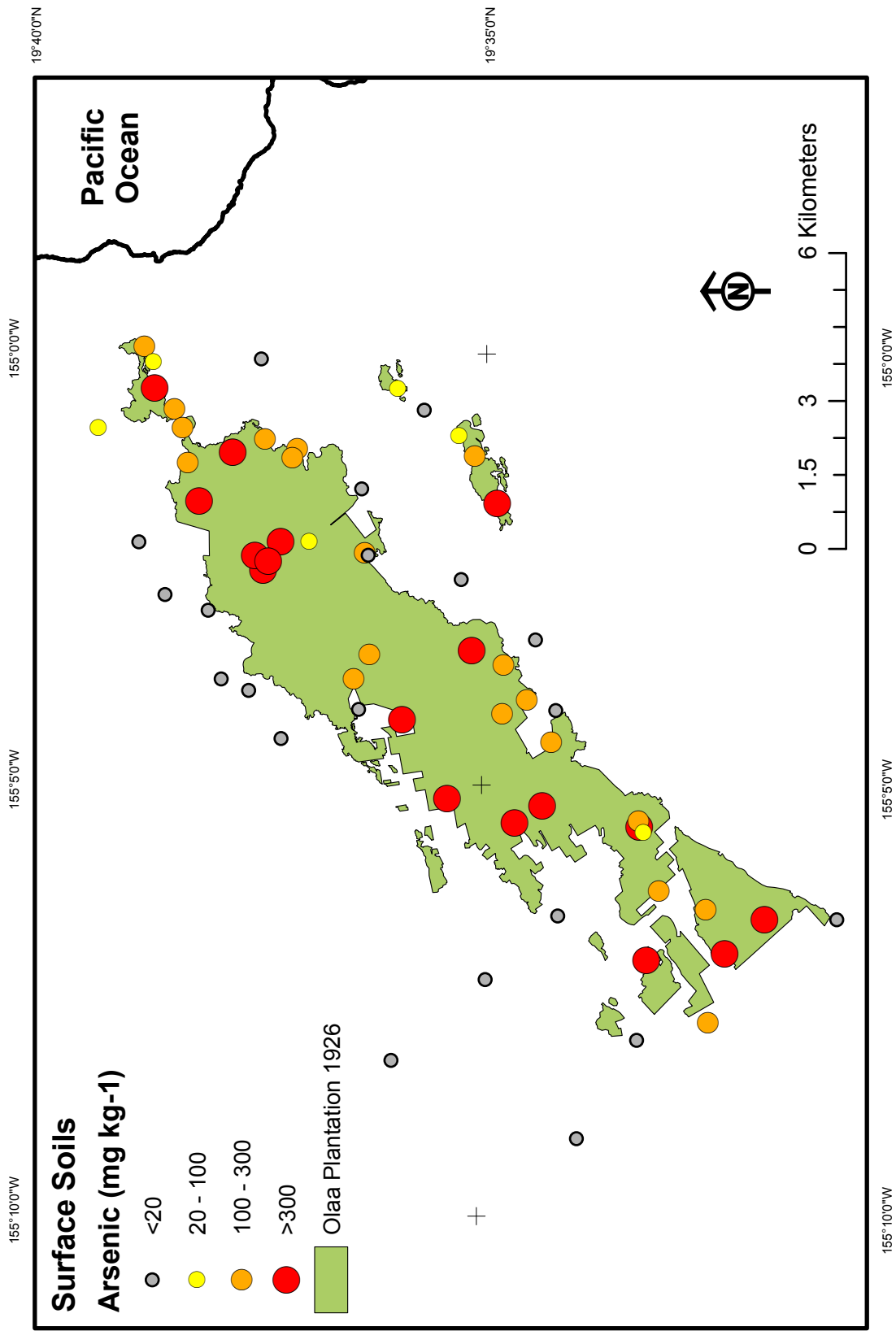


Figure 1.15 Soil arsenic concentrations across the former Olaa Sugar Plantation. Plantation extent from Cook (1926). Note that soil arsenic concentrations are elevated in nearly all locations where cane was cultivated.

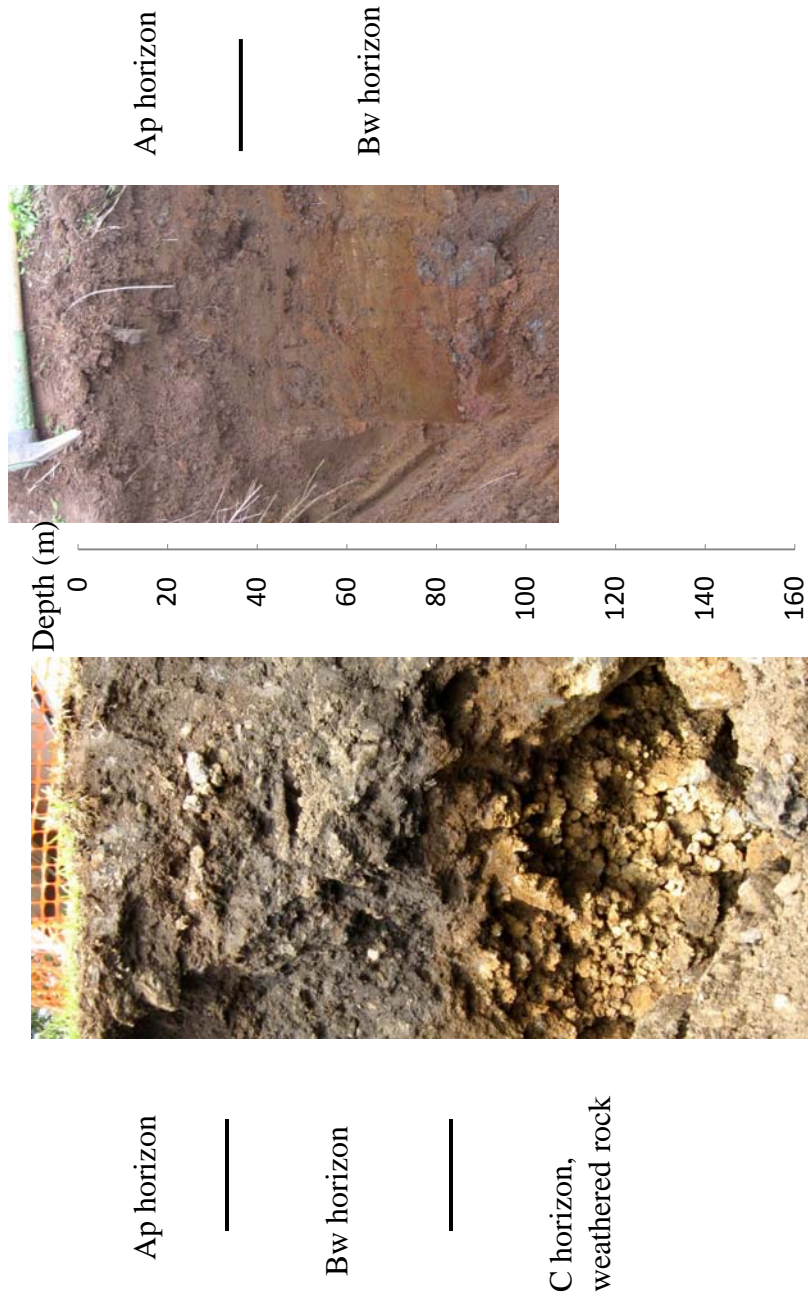


Figure 1.1.6 Photographs of Typic Hydrudands (left) and Acrudoxic Hydrudands (right) soil profiles. The Typic Hydrudands has high lithic content and dark gray-brown color due to accumulation of organic carbon. Underlying C horizon shows a “clinker zone” of a lava cobbles, with no soil development. Acrudoxic Hydrudands has lower lithic and organic content, and higher pedogenic Fe, than Typic Hydrudands.

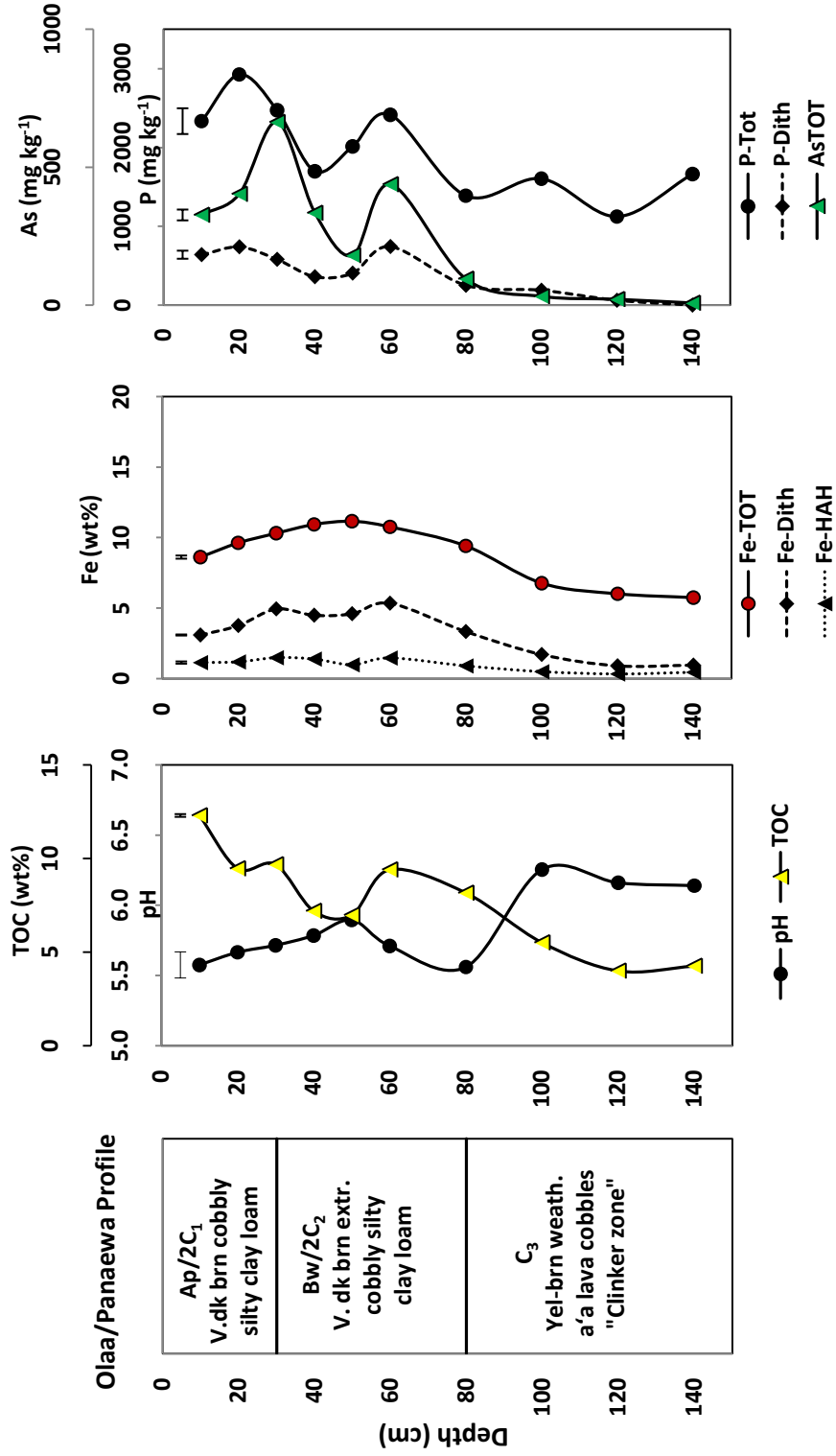


Figure 1.17 Vertical soil profile data for Lithic Hydruands. Note As_{TOT} and P_{Dith} (P_{CD}) have accumulated in 80 cm soil column, but are absent in underlying weathered rock. Data values provided in Table 1.5. Typical error bars, shown above data profiles, are 1 stdev for data points at 10 cm, based on coefficient of variance for replicate data analyses (see footnotes on Table 1.5).

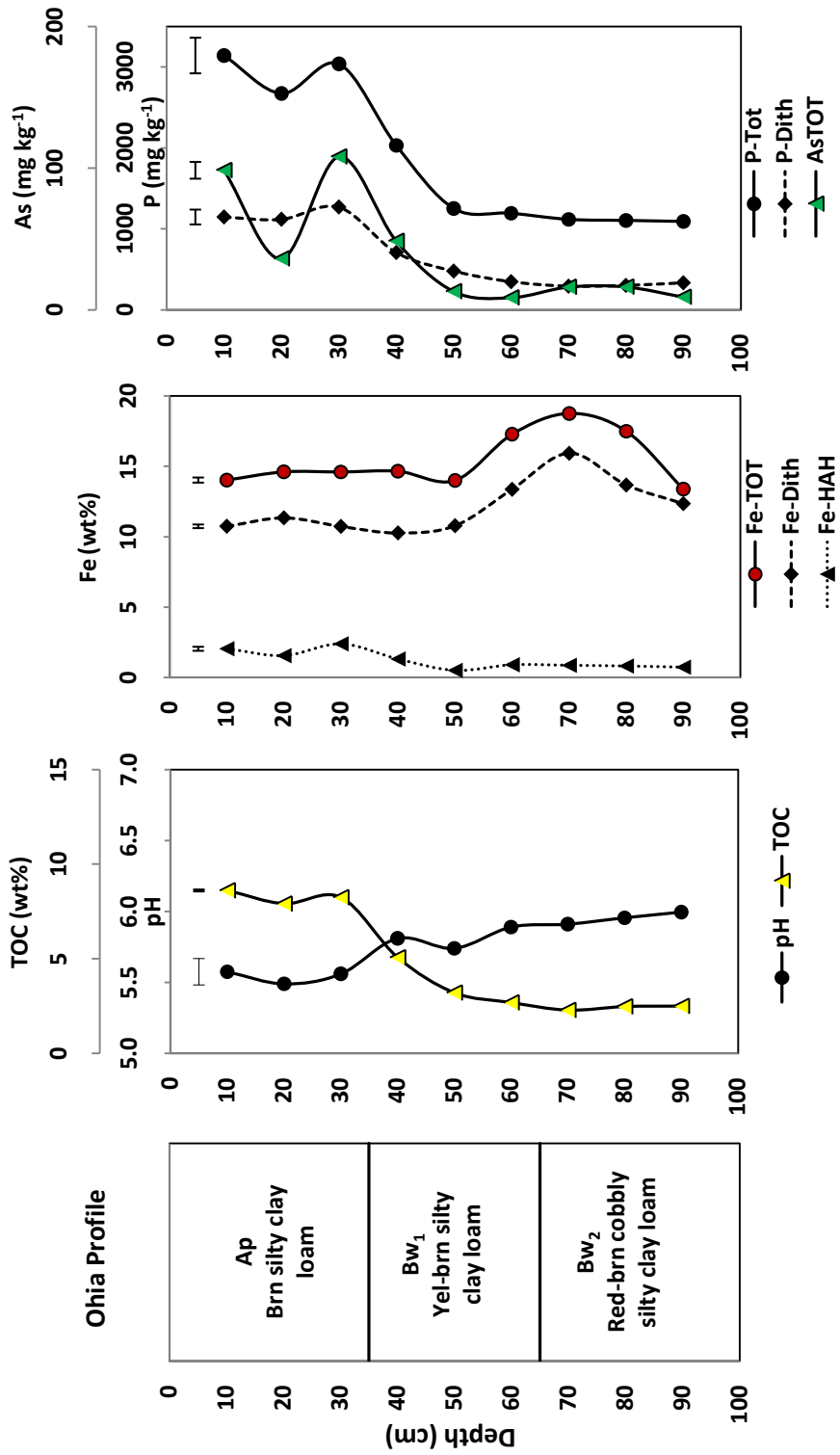


Figure 1.18 Vertical soil profile data for Acrudoxic Hydridands. Note that As_{TOT} and P_{TOT} appear to be co-located in soil profile, and do not extend below 50 cm at concentrations above background levels. Data values provided in Table 1.5. Typical error bars, above data profiles, are 1 stdev for data points at 10 cm, based on coefficient of variance for replicate data analyses (see footnotes on Table 1.5).

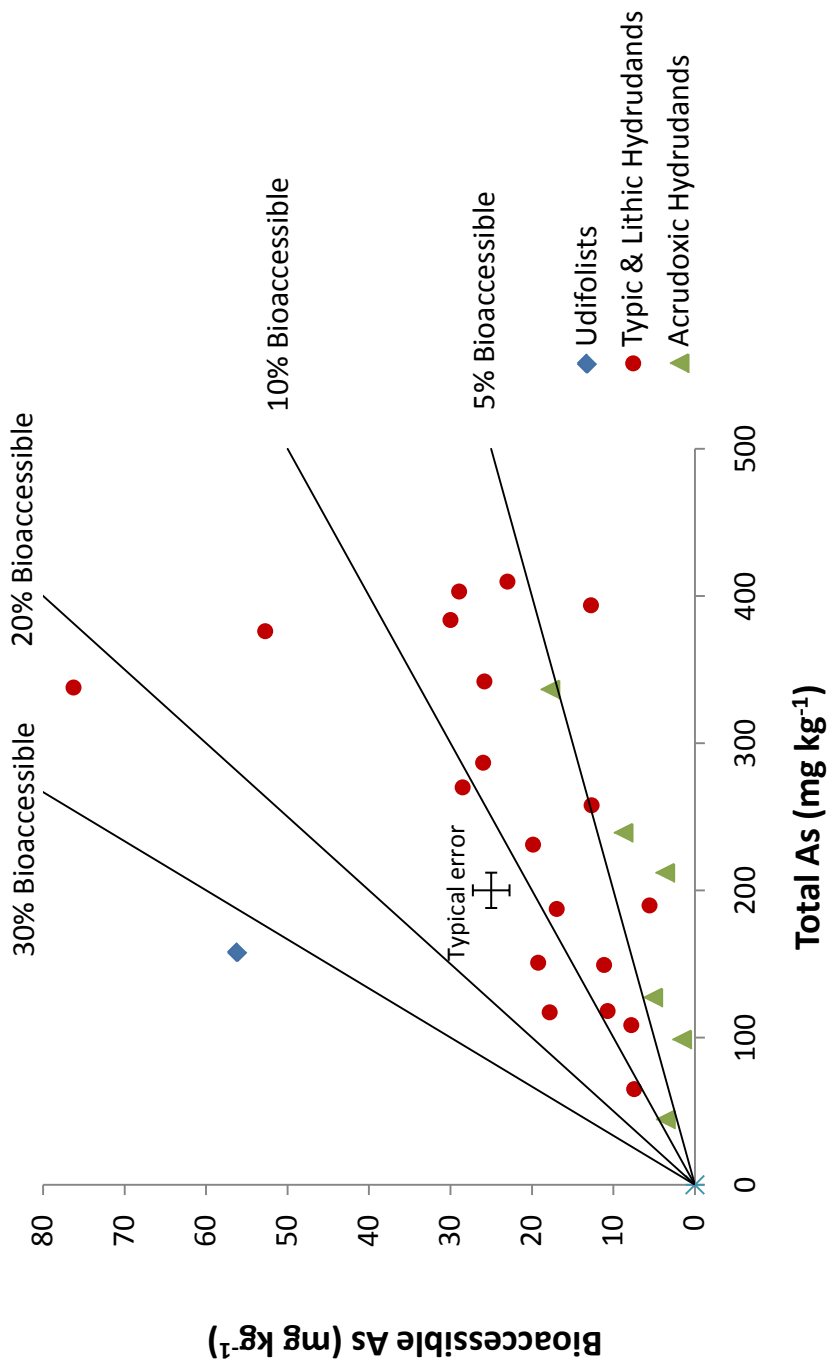


Figure 1.19 Cross-plot of total and bioaccessible arsenic in surface soils. Acrudoxic Hydrudands, with higher proportion of Fe oxyhydroxides and poorly crystalline aluminosilicates show lower percentage of bioaccessible As. Based on replicate analyses of NIST 2710 control soil, error (coefficient of variation) is 6% for As_{TOT} and 9% for As_{BAC} , as shown by “typical error” bars.

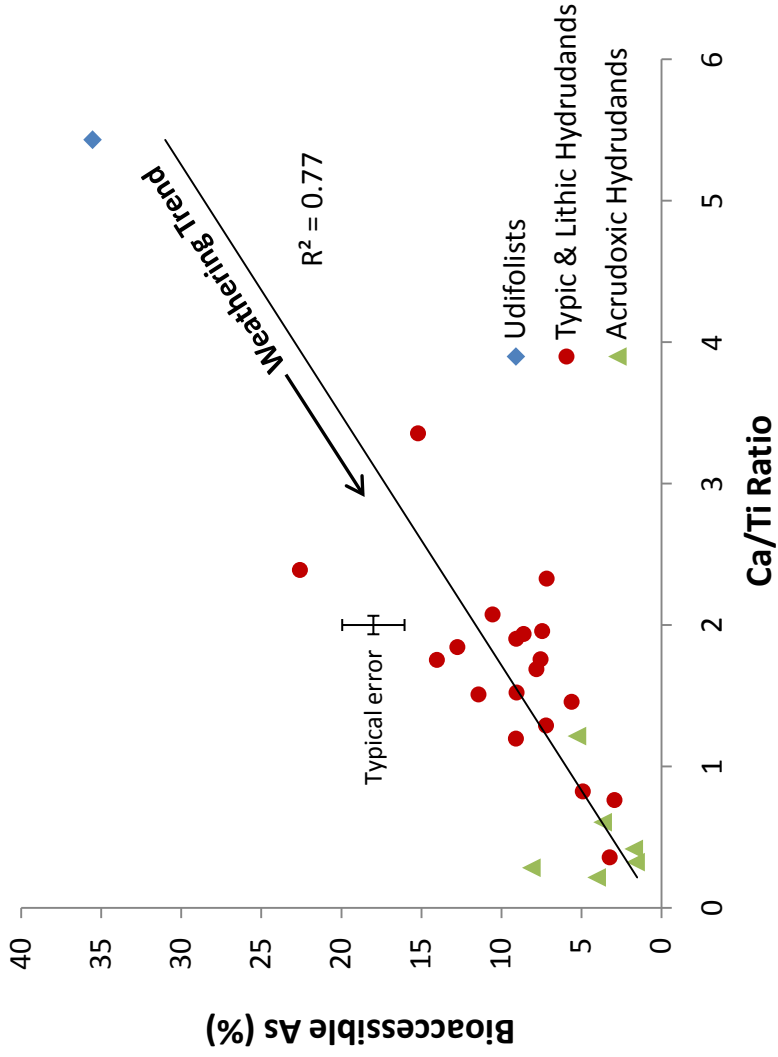


Figure 1.20 Cross-plot of Ca/Ti ratio and bioaccessible arsenic for surface soils. Udifolist soil, with poorly developed Fe oxyhydroxide and aluminosilicate secondary phases, shows highest Ca/Ti ratio and $As_{BAC\%}$. In contrast, more weathered Acrudoxic Hydrudands, with low Ca/Ti ratio show lower $As_{BAC\%}$. Typical error bars for $As_{BAC\%}$ are 11% coefficient of variation, CV) based on replicate analyses of NIST 2710 control soils. Error bars for Ca/Ti ratio are CV of replicate samples analyzed by EDXRF (errors propagated for fraction term).

Chapter 2. Soil Properties and their Influence on Arsenic Bioaccessibility

Abstract

Hawaiian Andisols developed from weathering of basalt lava and tephra are rich in pedogenic solid phases that strongly retain arsenic (As). *In vitro* bioaccessible As (AS_{BAC}) in historically-contaminated soils (N=72) from sugar cane fields and at chemical release sites on the Island of Hawaii, measured using the Solubility/Bioavailability Research Consortium (SBRC) gastric-phase test, ranges from <1% to 52% of total As. Total As (AS_{TOT}) and soil properties including pH, total organic carbon (TOC), total Fe, and reactive (citrate-dithionite (CD) and hydroxylamine hydrochloride extractable) Fe, Al, Si and P concentrations, were evaluated by multivariate linear regression modeling to predict AS_{BAC} . Two-variable models with total As as the first predictor variable and either total Fe, CD-extractable Fe or CD-extractable Al as the second predictor variables were able to explain 85-86% of the variability (R^2) in AS_{BAC} in soils with $<1000 \text{ mg kg}^{-1}$ AS_{TOT} , and 92% of the variability in all study soils. Addition of a third predictor variable to the linear regression provided no significant increase in predictive capability. Weathering of study soils and development of pedogenic solid phases with high specific sorption capacity for As oxyanions, such as Fe oxyhydroxides, allophane-like aluminosilicates and Al-humus complexes, results in generally low As bioaccessibility. In soils of similar composition, the percentage of AS_{BAC} significantly increased with total As loading. Phosphate content (CD-extractable) in study soils was not a significant predictor of AS_{BAC} , despite findings that addition of new phosphate increases AS_{BAC} . Simple field and laboratory methods were evaluated for use in predicting AS_{BAC} . Portable energy-dispersive X-ray fluorescence (EDXRF) instruments allow for rapid and cost effective determination of total As and Fe concentrations, which can be used in linear regression models to estimate AS_{BAC} . The use of reactive Fe (or Al) in regression equations to predict AS_{BAC} provides no improved accuracy, efficiency or cost advantage over the use of total Fe. Determination of reactive Fe content by targeted extraction is of similar effort and cost to direct measurements of AS_{BAC} using the SBRC-gastic (SBRC-g) *in vitro* test. We conclude that linear regression modeling of AS_{BAC} using total As and Fe soil concentrations are a cost effective screening tool, and should be considered in site assessments of As contamination in Fe-rich Andisols, along with direct measurement of AS_{BAC} by the SBRC-g *in vitro* method.

2.1 Introduction

Arsenic (As) can be toxic to humans and other biota under certain exposure scenarios. Most occurrences of As toxicity documented in human populations are the result of ingestion of drinking water with elevated As levels (Rahman et al., 2006). Incidental ingestion of soil with elevated As levels could potentially present a human health risk as

well, especially to sensitive populations such as children. Large tracts of former sugar cane lands in Hawaii have been shown to contain elevated soil As, primarily the result of application of arsenical herbicides during cane cultivation during the first half of the twentieth century (see Chapter 1).

The bioavailability of metals and metalloids in soil, sediment and solid waste is often considered in the estimation of potential human health risk. Not all As in soil is bioavailable, especially in soils or soil-like materials that have As incorporated into insoluble mineral phases, or have strong As binding capacity. USEPA (2007) and other environmental regulatory agencies have recognized the importance of considering the degree of bioavailability of metal contaminants in risk assessments and remedial action evaluations. The relative oral bioavailability of soil As in animal models (monkey and swine) has been shown to be highly variable, and in part controlled by soil mineralogy and geochemical conditions (Rodriguez et al., 2003; Roberts et al., 2007; Juhasz, 2007b). Bioavailability of soil As is a function of As speciation, solid-phase associations, and key soil properties (Scheckel and Chaney, 2009).

In lieu of costly animal studies of relative As bioavailability, a number of 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 As extracted in these *in vitro* tests is termed bioaccessible arsenic (AS_{BAC}). *In vitro* bioaccessibility may be a suitable predictor of relative As bioavailability (USEPA, 2007), particularly when validated with an *in vivo* animal study. Due to the complexity of chemical contaminants in soil substrates, multiple tools, including *in vitro* bioaccessibility assessments, are useful in supporting human exposure assessments (Schoof, 2004).

Studies of controls on AS_{BAC} in historically-contaminated soils typically look at a suite of soils with highly variable solid-phase properties, age, geography and type of As contamination. This approach is useful for developing a general understanding of the controls on AS_{BAC} , but is generally not useful for developing predictive models applicable to a specific contamination setting. The current study looks at soil As contamination in Andisols on the Island of Hawaii, within a suite of soils with similar provenance and age/type of As contamination. The principal study objective is to develop predictive models for estimating AS_{BAC} from soil properties that can be directly applied to the Hawaii soil As contamination problem. In addition, the study adds to our knowledge about controls on AS_{BAC} in Fe-rich volcanic-derived soils, a soil type prevalent in many regions of the world, particularly around the Pacific rim.

The current study area is the eastern portion of the Island of Hawaii, an area characterized by volcanic-derived soils historically used for sugar cane cultivation. Elevated As in these soils is the result of application or release of arsenical pesticides between 60 and

100 years ago (Hance, 1938). Study area soils are derived from basaltic lava and tephra, and taxonomically are of the Hydridands great group (USDA-NRCS, 2010). A continuum of soil properties are displayed in subject soils, due to variability in the proportion of lava rock, coarse tephra or ash parent material, and differential weathering history (see Chapter 1).

Previous Studies of Controls on Arsenic Bioaccessibility

The relationship between As bioavailability and soil properties has been investigated by several researchers, for example Roberts et al. (2007) evaluated 14 diverse U.S. soils for As bioavailability in a *Cynomolgus* monkey model, but did not find a strong association between soil properties and relative As bioavailability. However, the study only compared As bioavailability with the dominant As-bearing mineral phases, based on electron microprobe analysis, and did not consider other soil properties (pH, TOC, reactive Fe, etc). Studies that measured a number of key soil properties, beyond those evaluated by Roberts et al. (2007), have found that certain soil properties do influence AS_{BAC} . Yang et al. (2002) studied As adsorption, sequestration and bioaccessibility in a suite of 36 diverse U.S. soils representing seven soil orders (none were Andisols). They spiked study soils with soluble As(V) and measured AS_{BAC} at various time steps up to 6 months. Multivariate linear regression models were developed for the prediction of AS_{BAC} (on a percentage basis), using pH, cation exchange capacity, total organic carbon, total inorganic carbon, particle size, and reactive Fe and Mn (citrate-dithionite extractable) as predictor variables. They found that pH, reactive Fe content, and to a lesser extent total inorganic carbon, were the only significant predictors of As bioaccessibility. Sarkar and Datta (2004) artificially contaminated four soils with sodium arsenite and incubated them for 1 year. They found that soil properties, including reactive Fe and Al (oxalate extractable) and soil organic matter content, exerted control on As bioaccessibility. Pouschat and Zagury (2006) evaluated As-contaminated soils (N=12) around chromated copper arsenate-treated utility poles and observed a positive correlation between AS_{BAC} and organic carbon, and a negative correlation with clay content. Juhasz et al. (2007) evaluated controls on AS_{BAC} in a suite of Australian soils (N=50) contaminated with As from herbicide and pesticide use and from geogenic sources. They evaluated total element (As, Al, Fe and P) concentrations, pH and reactive (citrate-dithionite extractable) Fe as predictors of AS_{BAC} using linear regression models. The authors found that total As and either total or dithionite-extractable Fe successfully predicted the concentration of AS_{BAC} . Sarkar et al. (2006) evaluated the relationship of soil properties with As bioaccessibility in a set of soils (N=12) from sheep dipping sites in Australia and Florida. They found that AS_{BAC} was predicted in multivariate regression models by pH, total P, total Ca+Mg, electrical conductivity and clay content. In their study soils, oxalate-extractable Fe and Al and soil pH were not significantly correlated with AS_{BAC} , despite literature suggesting these components may strongly control As sorption and retention.

The nature of As association with solid phases is a key factor in bioavailability and bioaccessibility. At mining sites, where As may be occluded in sparingly soluble mineral phases, As mineral speciation and the dissolution properties of As-bearing minerals are critical in evaluating As bioavailability (Davis et al. 1996). In Fe-rich volcanic-derived soils contaminated by application of soluble arsenical pesticides, such as in the Hawaiian sugar cane soils of this study, As is dominantly sorbed onto pedogenic soil solid phases. In this situation, soil properties controlling As adsorption and desorption, such as the quantity of Fe oxyhydroxide and poorly crystalline aluminosilicates pedogenic phases, are key to its mobility in the environment, and are likely indicators of the degree of As bioaccessibility.

Solid-phase Properties of Hawaiian Andisols

Andisols are derived from volcanic lava and tephra, and exhibit a unique assemblage of pedogenic solid phases including Fe oxyhydroxides, allophanic materials (non-crystalline hydrous aluminosilicates), metal-humus complexes and opaline silica (Shoji et al., 1993). Reactive Fe and Al compounds in gels or short-range order forms predominate, and exhibit a high specific sorption capacity for oxyanions, such as phosphate and arsenite/arsenate. Iron in soils is generally more stable in oxyhydroxide 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 the soil solution tends to inhibit crystal growth of ferrihydrite, and leads to short-range order structure (Schwertmann, 1988). In organic-rich soils, humus preferentially complexes with Al, leaving little Al available to form aluminosilicates (Shoji et al., 1993). Humus complexed with Al or Fe is not readily biodegraded, and tends to accumulate in young Andisols. Allophane-like constituents are short-range order hydrous aluminosilicates characterized by a range of compositions and morphologies. Al-rich allophanes (Al:Si atomic ratio ~2:1) are most commonly observed (Parfitt and Kimble, 1989). Imogolite is a distinct aluminosilicate phase with a composition similar to Al-rich allophane, exhibiting 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, 1973; Jones and Fox, 1978). Gel materials in Hawaiian Andisols are composed of metal oxyhydroxides, aluminosilicates and associated organic compounds (Hudnall, 1977), have been shown to be very reactive towards phosphate (Jones and Fox, 1978), and are expected to have similar reactivity with As oxyanions.

Sorption and Sequestration of Arsenic in Soil

Inorganic As in oxic soil solutions is present as oxyanions, dominantly H_2AsO_4^- and HAsO_4^{2-} within the pH range of 3 to 10. Adsorption of As occurs predominantly on soil colloidal surfaces; these colloids can be oxides or oxyhydroxides of Al, Fe or Mn, aluminosilicates, calcium carbonates and organic matter (Sadiq, 1995). Many researchers

have investigated the sorption of As on iron oxides and oxyhydroxides. Iron oxyhydroxides have variable surface charge controlled by pH, degree of hydration, cation coordination and isomorphous substitution. The degree of As sorption may be in part dependent on surface charge of the iron oxyhydroxide sorbent (Sadiq, 1995). Specific adsorption (ligand exchange) is believed to be the dominant binding mechanism of inorganic As oxyanions onto iron oxyhydroxides (Hsia et al., 1994; Goldberg and Johnston, 2001). Bowell (1994) showed that arsenate (As(V)) displayed greater sorption than other As species across a broad range of pH typical in soils.

Ferrihydrite is a short-range order Fe oxyhydroxide and commonly the initial ferric solid phase precipitated in oxidized soils. Small particle size may be due to impedance of crystal formation by organics, silica or phosphate (Schwertmann, 1988). Ferrihydrite may transform to more crystalline Fe oxides, goethite and hematite, upon weathering and advancement of pedogenic processes. Arsenate adsorbs rapidly (within hours) onto ferrihydrite substrate, and achieves adsorption maxima of up to $0.25 \text{ mol}_{\text{As}} \text{ mole}_{\text{Fe}}^{-1}$ (Raven et al., 1998). Wilkie and Hering (1996) reported similar findings, that maximum adsorption density for As(V) on ferrihydrite is approximately $0.12 \text{ mol}_{\text{As(V)}} \text{ mol}_{\text{Fe}}^{-1}$. Arsenic retention at high concentrations in Fe-rich soils likely includes formation of ferric arsenate phases and is not solely a specific adsorption effect. Isotherms for As(V) adsorption to ferrihydrite are of the Langmuir type, showing adsorption limits due to surface saturation (Goh and Lim, 2003). X-ray adsorption fine structure studies of As(V) complexes on ferrihydrite and goethite at pH 6-8 indicate a dominance of inner-sphere bidentate binuclear complexes (Waychunas, 1993; Fendorf et al., 1997; Sherman and Randall, 2003).

Clay minerals (crystalline aluminum phyllosilicates) generally carry a net negative charge due to isomorphous substitution of Al and Si by cations of lower charge, and preferentially adsorb cations over anions. While not expected to be strong sorbents for As oxyanions, variably charged clays in acidic soils may contribute to As adsorption (Sadiq, 1995). In contrast to crystalline clay minerals, noncrystalline aluminosilicates such as allophane and imogolite are prevalent in young soils derived from volcanic ash, and may significantly contribute to As sorption and retention (Shoji et al., 1993). Based on the atomic arrangement of imogolite, which consists of gibbsite groups in outer sheets of tube-like structures (Cradwick et al., 1972; Gustaffson, 2001), a positive structural charge is present, resulting in high anion adsorption capacity (Gustaffson, 1998). The anion sorption properties of allophane-like nanoparticles have been evaluated for phosphate removal in water and wastewater (Yuan and Wu, 2007). Gustaffson (1998) showed strong adsorption of arsenate to synthetic imogolite, with an adsorption maximum between pH 4 and 8 and adsorption behavior similar to Al hydroxide/gibbsite. Extended X-ray absorption fine structure (EXAFS) analysis has revealed that As(V) sorption onto Al oxide surfaces is dominated by inner-sphere complexes with bidentate binuclear

bonding configurations (Arai et al., 2001), similar to the dominant As(V) binding mechanism to ferrihydrite.

Very few studies of As sorption by humus compounds or metal-humus complexes have been performed. For Andisols of Hawaii, humic matter is believed to be largely complexed with Al, and to a lesser extent Fe (Nanzyo, et al., 1993). Thanabalasingam and Pickering (1986) evaluated sorption of As(III) and As(V) on several humic substances, and found appreciable sorption capacity (up to 100 mmol As kg⁻¹). Studies of phosphate sorption to humus soils may provide an analogue to As. Giesler et al. (2005) measured significant phosphate sorption in high Al- and Fe-rich humus soils. Correlation of dissolved organic carbon (DOC) release with phosphate sorption was interpreted to be competitive displacement of DOC by phosphate in Al- and Fe-humus compounds. The degree of phosphate sorption in Andisols is generally determined by the concentration and form of reactive Al and Fe (citrate-dithionite or oxalate extractable) substrates, with lesser dependency on pH (Nanzyo et al., 1993). Further study of the role of metal-humus compounds on As retention and bioavailability is warranted.

In summary, pedogenic solid phase constituents of Hawaiian Andisols contain significant quantities of Fe oxyhydroxides, allophane-like aluminosilicates and metal-humus complexes, all of which are known to strongly adsorb oxyanions such as phosphate and arsenite/arsenate. Many of the soil properties responsible for As adsorption are believed to limit its release in animal digestive systems (bioavailability) and simulated human digestive systems (*in vitro* bioaccessibility tests). The quantity of pedogenic substrate in soil, believed to be largely responsible for binding As, can be estimated using targeted extraction techniques. The quantity of “reactive” Fe, Al and Si measured in targeted extractions will be evaluated for relevance in predicting AS_{BAC} .

Objective of Current Study

The effects of soil and contaminant geochemical properties on AS_{BAC} are not fully understood. Models for predicting AS_{BAC} have been developed for several suites of soils using a wide variety of soil properties as predictor variables. Findings of these studies (Yang et al, 2002; Juhasz, et al., 2007; Sarkar et al., 2007) are inconsistent, and in aggregate do not present a universal predictive model for determining AS_{BAC} from soil properties for all soil types. In addition, Andisols were not included in any of the previous studies evaluating controls on bioaccessible As. While developing a “universal model” for predicting AS_{BAC} in all soils is a valid objective, site-specific or regional level models for predicting AS_{BAC} for a particular As soil contamination setting, recognizing the limited range of soil properties for that setting, may be more useful in supporting site investigations and risk assessments.

Our study evaluates a suite of iron-rich volcanic-derived soils, displaying a continuum of soil properties and As contaminant concentrations, in order to better elucidate controls on

AS_{BAC} . Study soils are predominantly from large tracts of former sugar cane cultivation in the eastern portion of the Island of Hawaii that exhibit soil As concentrations from 50-1000 mg kg⁻¹, caused by a singular anthropogenic activity (arsenical herbicide application) occurring over a defined historical period (1913-1950). Naturally-occurring background levels of soil As in subject soils are <20 mg kg⁻¹ (USDA-NRCS, 2011). In addition to sugar cane cultivation areas, soils from several “chemical release” sites are included for study. The chemical release sites include an herbicide mixing plant, a chemical storage warehouse, and a canec (cane fiber board) manufacturing facility. Arsenic concentrations in chemical release site soils range from < 20 mg kg⁻¹ to more than 20,000 mg kg⁻¹. Arsenic historically applied to sugar cane and spilled at chemical release sites is believed to have been inorganic sodium arsenite (Hance, 1938).

In summary, the principal goals of this study are to determine the effects of soil properties and As contaminant loading on As bioaccessibility in Fe-rich Hawaiian soils, and to develop a predictive model for estimating AS_{BAC} for use in Hawaii and other similar soil/contaminant settings. A corollary study objective was to investigate the potential for simple field and laboratory methods to aid in the prediction of AS_{BAC} . Such tools could be used for initial estimates of AS_{BAC} and in large-scale data collection programs supported by *in vitro* bioaccessibility testing.

2.2 Methods

Study Area Soils, Collection and Laboratory Preparation

Surface soils were collected from spatially-distributed locations within former sugar cane plantation lands in the vicinity of the towns of Hilo, Kea’au, Mountain View and Pahoa on the eastern portion of the Island of Hawaii (Figure 1.2), and from chemical release sites in the southern and eastern portions of the Island of Hawaii. At each surface soil sample location, a composite sample was collected from the 0-20 cm depth interval (A horizon), starting at the top of mineral soil below surface organic matter (O horizon). Subsurface soils (Bw horizon) were collected from several test pits at 10 or 20 cm depth intervals to 1-2 meters below ground surface. All soil samples were air dried for 7 to 10 days, until daily moisture loss was less than 1%, sieved to <250 μm, and stored in sealed glass vials for subsequent testing.

In vitro Bioaccessible Arsenic

In vitro bioaccessibility assays can be used as a predictor of relative oral bioavailability of metal(loid)s (Ruby et al., 1996). *In vitro* test methods used to evaluate AS_{BAC} include the physiologically-based extraction test (PBET; Ruby et al., 1993), the in-vitro gastrointestinal model (IVG; Rodriguez et al., 1999), the method developed by the Solubility/Bioavailability Research Consortium (SBRC) (Kelley et al., 2002; Drexler and Brattin, 2007) and others. These methods typically consist of a gastric phase extraction at low pH, followed sequentially by an intestinal phase extraction conducted at near neutral

pH. For this study we have selected the gastric phase extraction of the SBRC test that has been correlated with *in vivo* (swine) relative As oral bioavailability for a suite of contaminated soils by Juhasz et al. (2007b).

The SBRC-g test consisted of extraction of 1 g of <250 µm air-dried soil in 100 mL of glycine-buffered HCl at pH 1.5, conducted at 37°C for a duration of 1 hour. An aliquot of extraction fluid was filtered through a 0.45 µm filter and analyzed for As by ICP-MS. Quality assurance/quality control procedures include blanks, blank spikes, matrix spikes, duplicate sample and control soil analyses (Drexler and Brattin, 2007). A second aliquot of soil was evaluated for total arsenic (As_{TOT}) by digesting soil in nitric, hydrochloric and hydrofluoric acid (Farrell et al., 1980), analogous to EPA Method 3052 (EPA, 2011), and analysis of the digest for As content by ICPMS. The percentage of As_{BAC} ($As_{BAC}\%$) is the mass of dissolved As in the *in vitro* extract divided by mass of As_{TOT} in the test soil times 100 (equation 1). The concentration of As_{BAC} is defined as the mass of dissolved As in the *in vitro* extract divided by the mass of the test soil (equation 2).

$$As_{BAC}\%(\%) = \frac{In\ vitro\ As\ (mg)}{Total\ As\ in\ soil\ (mg)} \times 100 \quad (1)$$

$$As_{BAC}\ (\mu g\ g^{-1}) = \frac{In\ vitro\ As\ (mg)}{Soil\ (kg)} \quad (2)$$

Laboratory precision of As_{TOT} and As_{BAC} measurements was determined by performing replicate analyses of both study soils and the National Institute of Standards and Technology (NIST) standard reference material (SRM) 2710 (Montana Soil, NIST SRM 2710). NIST SRM 2710 was run for As_{TOT} and As_{BAC} along with study soils in multiple lots (groups of samples run together) over a two year period, with results indicating a coefficient of variance³ (CV) of 6% for As_{TOT} (N=4) and 9% for As_{BAC} . These error measurements describe the analytical uncertainty in the laboratory methods across multiple sample lots. Replicate analyses of As_{TOT} and As_{BAC} were also conducted within a single laboratory sample lot, using four study soils and 7 replicates each. The observed error for As_{TOT} and As_{BAC} for intra-lot replicates averaged 2% and 7% CV, respectively. In addition to replicate analyses of study soils and NIST SRM 2710, laboratory QA/QC protocols for the SBRC-g test included duplicate analysis of As_{BAC} and As_{TOT} on at least 10 percent of samples, and analysis of blanks and matrix spikes. All analytical results utilized in this study were from sample lots meeting the QA/QC performance standards outlined in Drexler and Brattin (2007) for the SBRC-g test.

³ Coefficient of variation (CV) is the standard deviation divided by the sample mean, and is also referred to as the relative standard deviation (RSD)

Analysis of Soil Chemical Properties

Soil chemical properties were determined on splits of the <250 μm air-dried soil fraction evaluated for AS_{BAC} by the SBRC-g test. Soil pH was determined using a 1:1 soil:water slurry. Total organic carbon was measured using a Shimadzu TOC-V analyzer. Loss on ignition (LOI), designed to measure the sum of volatile constituents, principally water (residual free and bound) and organic compounds, was determined by soil mass differential before and after oven heating in a muffle furnace at 850°C for 8 h. Total element analysis (Ca, Ti, Fe, Sr, Zr) was conducted by energy-dispersive X-ray fluorescence (EDXRF) with a Bruker Tracer III-V instrument utilizing a rhodium-target x-ray tube and Al/Ti filters operating at 40keV. Spectra were collected over a 300 second acquisition time (five 60-second sweeps) with a PIN detector and 0.04 keV sampling bins. Raw spectra were processed using Bruker Artax software for removal of background. Calibration standards for EDXRF consisted of a subset of study soils analyzed for total element composition by EPA Method 3052 digestion and ICPOES.

Poulton and Canfield (2005) compared the efficacy of four targeted extraction techniques (Na acetate, citrate-dithionite, hydroxylamine hydrochloride and oxalate) for selective dissolution of common Fe minerals (Table 2.1). Their work demonstrated that the citrate-dithionite (CD) method (Raiswell et al., 1994) provided the most complete dissolution of secondary Fe minerals (ferrihydrite, lepidocrocite, goethite and hematite). Hydroxylamine hydrochloride (HAH) extraction (Chester and Hughes, 1967) targeted only the most reactive Fe forms: ferrihydrite and lepidocrocite. Ammonium oxalate (Phillips and Lovley, 1987) dissolved the pedogenic mineral phases ferrihydrite and lepidocrocite, however it also dissolved substantial magnetite, which is a primary igneous mineral in Hawaiian basalts, and had little or no effect on goethite and hematite. Sodium acetate (Tessier, 1979), principally a carbonate dissolution method, dissolved only a small fraction of ferrihydrite and lepidocrocite. Based on the findings of Poulton and Canfield (2005), we selected the HAH and CD targeted extraction methods for determination of reactive Fe in study soils. These extraction methods also dissolve some fraction of reactive Al and Si in soils; however, we are not aware of a comparative assessment of dissolution efficacy for specific Al-oxide and aluminosilicate mineral forms as performed by Poulton and Canfield (2005) for Fe oxides/oxyhydroxides. Phosphorus was analyzed in CD extracts to determine the potentially reactive fraction of P associated with the pedogenic iron oxyhydroxide phases. Details on reactive Fe targeted extraction methods are provided in Table 2.2.

2.3 Results and Discussion

Soil Properties and Analysis of Extent of Soil Weathering

Measured soil properties for all samples (N=72, <0.25 mm fraction) are provided in Table 2.3. The 0.25 mm fraction is used for *in vitro* bioaccessibility testing, therefore, the soil properties of this same fraction were measured to evaluate controls on AS_{BAC} .

These Andisol soils show a relatively narrow range of pH (5.2 to 7.5). TOC content is highly variable, ranging from 1.8% to 28.9%; highest in shallow soils (A horizon) and in soils developed over more recent lavas. LOI ranges from 12.1% to 50.7%, indicative of the high proportion of organics and hydrated mineral phases and gel materials in these Andisols. Total Fe ranges from 52 to 171 mg g⁻¹ and CD-extractable Fe (Fe_{CD}) ranges from 9 to 159 mg g⁻¹. Total Fe and Fe_{CD} are positively correlated (Figure 2.1), with low Fe_{CD} content reflecting immature surface soils or subsoils with much of the Fe present in partially weathered igneous minerals (olivine, pyroxene, magnetite, etc.). Progressive weathering of soils results in accumulation of pedogenic Fe phases including Fe oxyhydroxide and Fe-humus materials, and a corresponding increase in Fe_{CD} content. Total Fe (Fe_{TOT}) content increases as soils weather, indicating contraction of the soil profile without coincident loss in Fe content. In the most weathered Andisols, Acrudoxic Hydrudands, Fe_{CD} constitutes the majority of Fe_{TOT}, indicating nearly complete weathering of primary igneous mineral phases and development of pedogenic phases (2.1). HAH-extractable Fe (Fe_{HAH}) is significantly lower than Fe_{CD} in study area Hydrudands (see Figures 1.17 and 1.18), especially in the more weathered Acrudoxic Hydrudands, indicating that the majority of pedogenic Fe solid phases are not pure ferrihydrite (or lepidocrocite). These more recalcitrant Fe phases may be more crystalline Fe oxyhydroxides, such as goethite or hematite, or humus-complexed Fe phases (Shoji et al., 1993). Based on transmission electron microscopy, only small amounts of crystalline goethite and hematite were observed, therefore it is likely that the predominant Fe solid phases are poorly crystalline goethite and Fe-humus complexes.

Weathering processes modify the bulk elemental composition of the soil. Certain elements tend to accumulate as soils weather, while others become depleted. Of the major elements sourced by the parent basalt rock, Al, Ti, Mn and Fe accumulate, whereas Si, Na and Ca become depleted. For the major and trace elements readily measured by EDXRF (Ca and higher atomic numbers), Ti, Mn, Fe and Zr accumulate, whereas Ca, Ni and Sr become depleted (Figure 2.2). The ratio of a depleting to an accumulating element provides a useful indicator of the degree of volcanic soil weathering and element retention versus mobility (Chapter 1), and is more pronounced than changes observed for single elements. For example, the Ca/Ti ratio decreases with soil weathering and shows a strong inverse non-linear relationship with total and reactive Fe (Fe_{CD}) (Figure 2.3). As soils weather, calcium is readily leached, whereas Ti, Fe and other metals accumulate. The Ca/Ti ratio is a useful indicator of the degree of soil weathering, as it can be evaluated in both the field and laboratory by EDXRF. Calcium content in soil should be used with caution as an indicator of soil weathering or as part of a depleting/accumulating element ratio, as some plants may accumulate Ca leading to re-deposition at the top of the soil profile, and certain agricultural areas may have elevated Ca from lime applications. In older soils, Ti from atmospheric dust deposition may constitute a substantial fraction of the soil mass. In situations where Ca and Ti are not suitable for use, alternate element

ratios, such as Sr/Zr, may function better for estimating the degree of soil weathering (see Figure 2.2). In short, the Ca/Ti ratio appears to be useful as a general indicator of the degree of soil weathering in young Andisols of the study area.

Observed Arsenic Contaminant Loading

Naturally-occurring background levels of As in Hawaii soils are less than 20 mg kg⁻¹ (USDA-NRCS, 2011). Total As in former sugar cane surface soils (Ap horizon, 0-20 cm depth, <2 mm fraction) of the study area ranges from 40 to 670 mg kg⁻¹ with a mean value of 260 ±150 mg kg⁻¹ (see Table 1.4). Analysis of A_{TOT} from <0.25 mm soil fractions of former sugar cane soils, prepared for A_{BAC} analysis, ranged from 36 to 910 mg kg⁻¹ with a mean value of 260 ±150 mg kg⁻¹ (Table 2.3). Including soils collected from the chemical release sites, the range of A_{TOT} is much broader – up to 2.5 weight percent (25,000 mg kg⁻¹) in soils from a former herbicide storage facility. Bioaccessible As concentrations in former sugar cane soils range from <1 to 180 mg kg⁻¹, with a mean value of 28 ±34 mg kg⁻¹; and as high as 6900 mg kg⁻¹ in the most contaminated chemical release site soils. The percentage of A_{BAC} in study soils is also highly variable, ranging from 1.6% to 36%, with a mean value of 10 ±7% in sugar cane soils; and from 0.4% to 52%, with a mean of 10 ±11% for all study soils (Table 2.3). The relationship between A_{TOT} and A_{BAC} is shown on a Figure 2.4, displays poor correlation between these two parameters and demonstrates the need for better understanding of controls on A_{BAC}.

Controls on Bioaccessible Arsenic

The relationship between A_{BAC} and key soil parameters was examined using bivariate and multivariate linear regression analysis with the software program SAS[®] (SAS, 2008). Logarithmic (base 10) transformation of soil properties and As contaminant levels was performed to improve correlation coefficients, linearity, normality of residuals and homoscedasticity. Bioaccessible As (concentration form) was evaluated with respect to the following independent variables (predictors): pH, TOC, total As, total Fe, CD-extractable Al, Fe, Si and P, and HAH-extractable Al, Fe and Si. Bivariate regressions were performed between A_{BAC} and each predictor variable for all samples with A_{TOT} less than 1000 µg g⁻¹ (Table 2.4). Samples with A_{TOT} greater than 1000 µg g⁻¹ were excluded from initial evaluation, to minimize the influence of a few (N=9) more highly As-contaminated samples on the analysis. Three independent variables correlated with log A_{BAC} with correlation coefficients (R²) greater than 0.30: log A_{TOT} (positively correlated, R² = 0.67), log Fe_{CD} (negatively correlated, R² = 0.31), and log Si_{CD} (negatively correlated, R² = 0.55). Even though samples with A_{TOT} >1000 µg g⁻¹ were not included in regression models, log A_{TOT} was the strongest predictor of log A_{BAC}. The regression equation for the best single predictor model for estimating A_{BAC} is:

$$\log A_{BAC} = (1.31 \times \log A_{TOT}) - 1.88 \quad (3)$$

[note: A_{BAC} and A_{TOT} in mg kg⁻¹]

A statistical summary of all predictive models is provided in Table 2.4, and a cross-plot demonstrating the predictive capability of the single predictor model using equation (3) is provided in Figure 2.5. The regression equation (3) in non-logarithm form describes a power function with coefficient >1 , meaning A_{SBAC} increases at a greater rate than A_{STOT} . Therefore, higher percentages of A_{SBAC} (A_{SBAC}/A_{STOT}) are anticipated at higher total As loading rates.

Total Fe Al_{CD} , Fe_{CD} , and Si_{CD} are negatively correlated with A_{SBAC} , but with poorer capability to predict A_{SBAC} than A_{STOT} . Iron oxyhydroxides and aluminosilicates are believed to have a direct role in binding As oxyanions, and increasing amounts of these substrates may reduce bioaccessible As. Various soil parameters are indicative of the concentration of these adsorptive substrates, including Fe_{TOT} and CD and HAH-extractable Fe, Al and Si. None of these parameters alone is a strong predictor of A_{SBAC} . Surprisingly, HAH-extractable Al, Fe and Si, showed no correlation with A_{SBAC} . CD-extractable P, which might compete with As for sorption sites, and was hypothesized to be positively correlated with A_{SBAC} , showed no correlation (Table 2.4).

Two-variable linear regression models were constructed using A_{STOT} as the primary predictor and each of the other variables. Three models provided regression correlation coefficients (R^2) of 0.80 or greater (Table 2.4). The model with highest R^2 (0.86) included A_{STOT} and Fe_{CD} as predictors, as shown in equation (4).

$$\log A_{SBAC} = (1.19 \times \log A_{STOT}) - (1.14 \times \log Fe_{CD}) + 0.26 \quad (4)$$

[note: A_{SBAC} and A_{STOT} in $mg\ kg^{-1}$, Fe_{CD} in $mg\ g^{-1}$]

Models using [A_{STOT} , Fe_{TOT}] or [A_{STOT} , and Al_{CD}] were nearly as successful at predicting A_{SBAC} as the [A_{STOT} , Fe_{CD}] model, with R^2 values ranging from 0.83 to 0.85. Three variable models were assessed using various regression techniques (stepwise, maximum R^2 improvement, etc.), however the addition of a third independent variable made no appreciable improvement in model prediction (no R^2 improvements greater than 0.01 compared to 2-variable models). Because of increased model complexity, and minimal improvement in model prediction, use of 3-variable models is not warranted.

Regressions using all study data, not just those with $A_{STOT} < 1000\ mg\ kg^{-1}$ (9 additional samples) resulted in similar linear regression equations with slightly higher correlation coefficients (Table 2.4). Consistent with the results of bivariate regressions, pH, TOC and P_{CD} provide no support in predicting A_{SBAC} in multivariate regressions, whereas HAH-extractable Al, Fe and Si provided only minimal model improvements. In summary, A_{SBAC} in study soils is best predicted by A_{STOT} coupled with either Fe_{TOT} or CD-extractable Fe or Al in a two predictor variable model.

Comparison with Other Modeling Studies

Our findings are generally consistent with the regression modeling of Juhasz et al. (2007a), who determined that the concentration of AS_{BAC} in contaminated soils was best predicted by total As and either total or CD-extractable Fe. Juhasz et al. (2007a) measured total P for study soils, but did not find it to have an effect on AS_{BAC} . Yang et al. (2002) in their study of the influence of soil parameters on As bioaccessibility in a suite of laboratory-contaminated soils did not evaluate P content in their models. In this study, we chose to measure and model CD-extractable P, which is associated with the reactive Fe fraction and may compete with As for sorption sites. For most soil-like materials, the sorption behavior of inorganic P and As has been shown to be similar (Roy et al., 1986; Manning and Goldberg, 1996). Phosphate has been shown to compete with As for sorption on iron oxide surfaces (Jackson and Miller, 2000; Jain, 2000). Phosphate addition to one of the soils in this study (see Chapter 3) significantly increased AS_{BAC} ; the addition of 1.5 mg g^{-1} P to the $<2 \text{ mm}$ soil fraction (2 to 3 times more concentrated in the $<250 \text{ }\mu\text{m}$ fraction) increased the concentration of AS_{BAC} from approximately 30 to 70 mg kg^{-1} . The current study did not reveal a significant control on AS_{BAC} by CD-extractable P, which ranged from 0.1 to 4.5 mg g^{-1} in soils with $AS_{TOT} < 1000 \text{ mg kg}^{-1}$. It appears that the P_{CD} in study soils, which may be from both naturally-occurring and anthropogenic sources (P fertilizers) does not affect AS_{BAC} . Walker and Syers (1976) describe the evolution of P in soils over time, noting that initially reactive P adsorbed to soil mineral surfaces tends to become occluded in crystalline Fe and Al oxides over time, reducing its reactivity and bioavailability. Although new phosphate added to study soils dramatically increases AS_{BAC} , we suggest that naturally-occurring P, and P introduced by fertilization some 30 to 100 years ago, is largely occluded and has little or no affect on AS_{BAC} .

Yang et al. (2002) developed a two variable model based on a suite of 36 soils, in which the percentage of AS_{BAC} was predicted by pH (CaCl_2 solution) and reactive Fe content (citrate-dithionite-bicarbonate method, Fe_{CDB}) [they also developed a 3 predictor variable model using pH, Fe_{CDB} and total inorganic carbon]. Their two-variable regression model is:

$$AS_{BAC}\% = (11.3 \times \text{pH}) - (30.5 \times \log Fe_{CDB}), R^2 = 0.74 \quad (5)$$

Application of the Yang et al. (2002) regression model to our data results in poor prediction of $AS_{BAC}\%$ (Figure 2.6). It should be noted that pH and reactive Fe extraction methods of our study are not identical to those performed by Yang et al. (2002) (although *in vitro* bioaccessibility tests were essentially the same), which may be responsible for some of the variance between the Yang-predicted and observed $AS_{BAC}\%$ values. In addition, the soils evaluated by Yang were artificially contaminated with As and cured up to 6 months, in contrast to the soils of this study that were contaminated 60 to 100 years ago.

In their study of 50 Australian soils, Juhasz et al. (2007) developed several multivariate linear regression models to predict AS_{BAC} in concentration form. The regression model for all soils, using AS_{TOT} and Fe_{TOT} as predictors is:

$$AS_{BAC} = (0.409 \times AS_{TOT}) - (4.759 \times Fe_{TOT}) + 67.85, R^2 = 0.955 \quad (6)$$

Application of the above regression model to our study soils, again results in a poor prediction of AS_{BAC} (Figure 2.7). There may be several reasons that the regression models developed from the previous studies fail to accurately predict AS_{BAC} in the Hawaiian Andisols of the current study. Neither of the previous studies included Andisols, which have unique properties including high concentrations of reactive Fe oxyhydroxides and aluminosilicates. In particular, the current study soils have a more limited range of pH and a higher range of reactive Fe than soils from the Yang and Juhasz studies (Figure 2.8). Soil pH in current study soils (dominantly Andisols) appears to have no influence on AS_{BAC} , whereas using the Yang regression model, a change in pH by one standard unit results in an 11% change in $AS_{BAC}\%$. This strong pH effect on AS_{BAC} was simply not observed in our study soils. The Juhasz model generally underpredicts AS_{BAC} in Hawaiian Andisols, by ascribing a stronger negative effect from Fe_{TOT} content than determined in our regression models. In summary, we believe the soil properties of the Fe-rich Hawaiian Andisols, and their relationship to AS_{BAC} , are not adequately described in regression models from prior studies. We believe that accurate predictive models for AS_{BAC} in most settings will be best achieved using project-specific models. At present, a universal model for predicting AS_{BAC} based on As contaminant levels and key soil properties has not been developed.

Effect of Total Arsenic Loading and Reactive Fe Content on Bioaccessible Arsenic

At one of the chemical release sites, soil AS_{TOT} concentrations vary more than 3 orders of magnitude, and provide a unique opportunity to evaluate the effects of AS_{TOT} loading on AS_{BAC} in soils of similar composition. There are two distinct soil horizons at the site, within an Fe-rich Acrudoxic Hydruclands. An upper A Horizon soil is organic-rich (TOC 8.4 wt %) with Fe_{TOT} of 115 mg g⁻¹ and Fe_{CD} of 78 mg g⁻¹, and an underlying B Horizon that exhibits lower TOC content (3.1 wt %) and higher Fe_{TOT} and Fe_{CD} content (140 mg g⁻¹ and 109 mg g⁻¹, respectively). The relationship between AS_{BAC} and AS_{TOT} for A horizon (n=7) and B horizon (n=5) soils is clearly non-linear, with significantly higher percentages of AS_{BAC} at higher AS_{TOT} loadings (Figure 2.9). Increased $AS_{BAC}\%$ at higher As loading rates has been observed by other workers, including Yang et al. (2003). For the A Horizon soils, $AS_{BAC}\%$ ranged from 1.5 to 37 percent across the AS_{TOT} range of 46 to 19,000 mg kg⁻¹. B horizon soils, with higher reactive Fe content than A horizon soils, show lower concentrations of AS_{BAC} than A horizon soils at similar AS_{TOT} loadings reflecting the increased binding capacity of the more Fe-rich soils.

The non-linear relationship between A_{STOT} and A_{SBAC} is described by a power function in which $A_{SBAC} = a \cdot A_{STOT}^b$. A similar relationship has been observed in As sorption isotherms of Hawaiian Andisols (Chapter 1) in which non-linear partitioning between solid and aqueous phases was observed (Figure 2.10). Arsenic sorption isotherms were prepared using two soils exhibiting very different Fe_{CD} content (35 and 120 mg g⁻¹). Significantly higher sorption capacity was observed for the high Fe_{CD} soil, and both soils showed less complete (lower percentages of) sorption at high As loading rates. Soil properties that control the affinity of As adsorption (principally reactive Fe content) are believed to similarly limit As desorption within the *in vitro* SBRC-g test. Soils with high As loading show higher $A_{SBAC\%}$, which may reflect finite limits of As sorption sites. Alternatively, at higher As loadings, As may form ferric arsenate mineral associations (Raven et al., 1998) that are preferentially dissolved in the SBRC-g test as compared to Fe-oxide and aluminosilicate adsorbed As.

As described above for the chemical release site, which has two distinct soil types and As contaminant concentrations that vary over 3 orders of magnitude, the effects of Fe content and A_{STOT} loading on A_{SBAC} can be directly observed in site data. The linear regression model for predicting A_{SBAC} , utilizing A_{STOT} loading and Fe content (Fe_{TOT} or Fe_{CD}) as predictors, provides further insight into these controls on A_{SBAC} . The effect of each model predictor (a control on A_{SBAC}) is readily observed by considering the second predictor constant. To observe the effect of Fe_{CD} content on A_{SBAC} , we hold A_{STOT} constant and plot the relationship of Fe_{CD} to $A_{SBAC\%}$. A class of curves for A_{STOT} fixed at 50, 500 and 5000 mg kg⁻¹ (Figure 2.11) shows that $A_{SBAC\%}$ is strongly controlled by reactive Fe content, and percentages of A_{SBAC} at constant As loading can be quite high (>50%) in soils with less than 40 mg g⁻¹ of Fe_{CD} . On the other hand, soils with high Fe_{CD} content, above 100 mg g⁻¹, will have A_{SBAC} below 15% even at A_{STOT} loading of several thousand mg kg⁻¹.

The effects of A_{STOT} loading on a soil of constant composition can be evaluated by plotting A_{STOT} against $A_{SBAC\%}$ at constant Fe_{CD} content (Figure 2.12). The influence of A_{STOT} on $A_{SBAC\%}$ is strongest in soils with low Fe_{CD} content, and at lower A_{STOT} loadings. Most of sugar cane soils of the study area are Typic or Lithic Hydruclands, with average Fe_{CD} content about 60 mg g⁻¹. Based on our linear regression model (Equation 4) for such a soil, $A_{SBAC\%}$ would be 7.1% at A_{STOT} of 100 mg kg⁻¹, but would increase to 14.5% at A_{STOT} of 1000 mg kg⁻¹. The significance of the non-linear relationship between A_{STOT} and A_{SBAC} should not be overlooked. In conventional deterministic risk assessments, relative bioavailability of a compound (such as arsenic) for the oral route of exposure, also termed the relative absorption factor (RAF), is used to modify exposure or intake estimates to account for limited bioavailability (USEPA, 1989; Schoof, 2004). *In vitro* bioaccessibility is commonly used to estimate relative bioavailability or RAF. In site-specific risk assessments, the RAF for a compound in a particular media (such as As in

soil) is typically treated as a constant. As we have shown, at sites with highly variable soils, or a wide range of A_{STOT} concentrations, $A_{SBAC\%}$ is variable – and a single RAF value may not be appropriate to capture the variability in site soils and allow precise estimates of risk.

Streamlining Investigations of Bioaccessible Arsenic

Rapid and cost effective methods for estimating A_{SBAC} could improve site investigations, risk assessments, remedial designs and mitigations at many As-contaminated sites. Certain field projects require estimation of A_{SBAC} for a large number of samples, for example in site investigations and remedial design activities where the As soil cleanup criterion is based on a A_{SBAC} concentration, as is typical in Hawaii (HDOH, 2006; 2010). Predictions of A_{SBAC} in soils can be made using total element concentrations as predictors in multivariate linear regression models. Total elemental analysis can be performed by traditional laboratory methods such as acid extractions (EPA methods 3050B, 3051 and 3052) coupled with ICP analysis of extracts (EPA 6010 or 6020). Alternatively, field portable EDXRF instruments can provide rapid and cost effective elemental analysis to support such evaluations. Soil preparations (drying, sieving and grinding) and use of site-specific standard reference materials need to be carefully considered in order to generate accurate elemental analyses using EDXRF (Kalnicky and Singhvi, 2001; Ge et al., 2005; Tjallingii et al., 2007). As described above, multivariate linear regression models to predict A_{SBAC} using As and Fe as predictor variables can be quite accurate. A two variable models using A_{STOT} and Fe_{TOT} as independent variables predicted A_{SBAC} nearly as well as models including Fe_{CD} or Al_{CD} . The advantages of working with total element concentrations obtained with cost effective analytical procedures makes this approach useful for many site investigation and remediation applications.

Some workers (Yang et al., 2002) have suggested that the use of predictive models based on soil properties could provide rapid and inexpensive preliminary bioavailability estimates at contaminated sites. This study, as well as the findings of Yang et al. (2002) and Juhasz et al. (2007) indicate that reactive Fe is a key predictor of A_{SBAC} . Laboratory methods for measuring reactive Fe, whether by the citrate-dithionite targeted extraction method or others (i.e. hydroxylamine hydrochloride or ammonium oxalate) are of similar complexity and cost as direct measurement of A_{SBAC} by the SBRC-g method. Therefore, no advantage is gained by measuring reactive Fe and developing a prediction model for A_{SBAC} , when for the same effort and cost A_{SBAC} can be directly measured using an *in vitro* test. Commercial laboratories in the U.S. currently offer analysis of A_{SBAC} by SBRC-g at competitive pricing.

2.4 Conclusions

This study improves our understanding of the role of key soil properties on A_{SBAC} , and presents predictive models for estimating A_{SBAC} in Fe-rich volcanic-derived soils on the

Island of Hawaii. Predictive models developed for these study soils are not necessarily recommended for use in other As-contamination scenarios without further refinement.

Soils of the eastern portion of the Island of Hawaii are dominantly of the Andisol Order, and have elevated As levels due to use of arsenical herbicides from 1913 to 1950. Andisols have a pedogenic solid phase fraction consisting of Fe oxyhydroxides (such as ferrihydrite and goethite), short-range-order aluminosilicates (allophanes) and metal-humus compounds. These pedogenic phases strongly adsorb As and limit its release in bioaccessibility tests. Soils have a narrow range of pH, from 5.2 to 7.5; and wide variation in TOC (1.8 to 25.9 wt %). Total Fe varies from 28 to 171 mg g⁻¹, whereas reactive (citrate-dithionite extractable) Fe ranges from 9 to 159 mg g⁻¹. Soils show a progression from lower to higher Fe and Al content as weathering progresses, indicative of accumulation of Fe oxyhydroxide and aluminosilicate pedogenic phases. Total As in former sugar cane fields ranges from 36 to 906 mg kg⁻¹, and up to 25,000 mg kg⁻¹ in soils at chemical release sites.

As_{BAC} (concentration basis) is well predicted by way of 2 variable linear regression models, with As_{TOT} as the first predictor variable and either Fe_{TOT}, Fe_{CD} or Al_{CD} as the second predictor. Regression equations for soils with As_{TOT} <1000 mg kg⁻¹ explain 86% of the variance in As_{BAC}, and 91% of variance for all study soils. Addition of a third independent variable does not improve model prediction. Results of this study are generally consistent with previous studies of controls on As_{BAC} (Yang et al. 2002, Juhasz et al. 2007), however pH was not observed to exert control on As_{BAC} as observed by Yang et al. (2002). Neither of these previous studies included Fe-rich volcanic-derived Andisols, and therefore previous regression models do not adequately predict As_{BAC} in our study soils. Accurate predictive models for As_{BAC} will likely require use of data from the specific study area of interest, or very similar soil types and As contamination histories.

Total As loading and Fe content are not linearly related to As_{BAC}. At sites with a large range of As_{TOT} concentrations, or with variable soil properties, As_{BAC} as expressed on a percentage basis of As_{TOT} may also be highly variable. Single point estimates of As_{BAC}% for use in deterministic risk assessment calculations may not adequately describe site conditions and potential risks. Rapid and cost effective estimates of As_{BAC} can be made by measuring As_{TOT} and Fe_{TOT} using EDXRF, and applying the linear regression model to predict As_{BAC}. The authors have successfully employed this approach at numerous sites in Hawaii. Direct measurements of As_{BAC} are recommended over use of predictive models for most site investigations and remediation projects, except in situations where a large number of estimates of As_{BAC} are needed or costs for *in vitro* bioaccessibility testing are excessive.

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Table 2.1 Comparison of Targeted Dissolution Techniques for Common Iron Minerals From Poulton and Canfield (2005)

Mineral	Formula	Na Acetate ^a	Percent Removal (for optimal extraction times)		
			HAH ^b	Dithionite ^c	Oxalate ^d
Ferrihydrite	Fe ₅ HO ₈ ·4H ₂ O	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 ₂ O ₃	0%	0%	94%	0%
Magnetite	Fe ₃ O ₄	0%	0%	7%	100%

Notes:

From Poulton and Canfield (2005)

^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 (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 2.2 Targeted Iron Mineral Dissolution Methods

	Citrate-Dithionite Method ^a	Hydroxylamine Hydrochloride Method ^b
I. Sample Preparation	Air dry or oven dry soil at 40°C Sieve <0.25mm, finely ground	Air dry or oven dry soil at 40°C Sieve <0.25mm, finely ground
II. Reagents	50 g/L sodium dithionite, 58.82 g/L sodium citrate, 20 mL/L acetic acid solution	1M Hydroxylamine-HCl in 25% v/v acetic acid solution
III. Solution : Soil Ratio	150:1	100:1
IV. Procedure	Place ~80mg sample in 15mL centrifuge tube Add 12mL fresh reagent mixture Agitate @ 21°C for 2 hrs Centrifuge @ 2000 g for 5 minutes Decant, filter 0.45µm	Place ~100 mg sample in 15mL centrifuge tube Add 10mL fresh reagent mixture Agitate @ 21°C for 48 hrs Centrifuge @ 2000 rpm for 5 minutes Decant, filter 0.45µm
V. Analysis	Measure Fe, Ti, Al, Si, P by ICP-OES	Measure Fe, Ti, Al, Si by ICP-OES
VI. Target Fe Phases	Ferrihydrite, Goethite, Hematite	Ferrihydrite

Notes:

^a Poulton and Canfield (2005) after Raiswell et al. (1994) after Mehra and Jackson (1960) and Lord III (1980)

^b Poulton and Canfield (2005) after Chester and Hughes (1967)

Table 2.3 Soil Properties, <0.25mm fraction, air-dried basis

Sample ID	Taxonomy	Series	Depth ^a (cm)	Site Use ^b	pH ^c	TOC ^d (wt%)	As _{BAC} ^e (mg kg ⁻¹)	As _{TOT} ^f (mg kg ⁻¹)	As _{BAC} ^g (%)	Fe _{TOT} ^h (mg g ⁻¹)	Ca _{TOT} ⁱ (mg g ⁻¹)	Ti _{TOT} ^j (mg g ⁻¹)	Ca/Ti ^k Ratio	Al _{CD} ^l (mg g ⁻¹)	Fe _{CD} ^m (mg g ⁻¹)	Si _{CD} ⁿ (mg g ⁻¹)	P _{CD} ^o (mg g ⁻¹)	Al _{HAF} ^p (mg g ⁻¹)	Fe _{HAF} ^q (mg g ⁻¹)	Si _{HAF} ^r (mg g ⁻¹)
1	Acrodoxic Hydruudands	Ohia	10	SC	5.6	8.6%	1.6	99	1.6%	139	7.9	24	0.3	35.9	107	3.7	1.1	32.0	19.4	8.4
2	Acrodoxic Hydruudands	Ohia	20	SC	5.5	7.9%	0.7	36	1.9%	143	6.2	25	0.2	36.8	113	4.0	1.1	32.7	14.7	9.0
3	Acrodoxic Hydruudands	Ohia	30	SC	5.6	8.2%	2.3	110	2.1%	138	7.1	24	0.3	37.1	107	3.4	1.3	33.7	23.4	8.6
4	Acrodoxic Hydruudands	Ohia	40	SC	5.8	5.1%	1.0	49	2.1%	152	3.2	27	0.1	32.0	103	3.2	0.7	33.4	12.4	10.4
5	Acrodoxic Hydruudands	Ohia	70	SC	5.9	2.3%	<1	16	1.2%	171	1.2	34	0.04	39.0	159	7.7	0.3	29.8	8.2	10.5
6	Typic Hydruudands	Panaewa	0-20	SC	5.6	11.1%	30	380	7.8%	99	23	14	1.7	17.1	42.6	1.5	1.0	28.9	12.5	8.4
7	Typic Hydruudands	Olaa	0-20	SC	5.7	12.4%	76	340	23%	88	30	13	2.4	15.0	32.6	1.2	1.8	30.6	9.3	9.2
8	Typic Hydruudands	Olaa	0-20	SC	5.8	11.8%	26	290	9.1%	70	20	10	1.9	16.2	38.0	1.5	1.0	26.3	12.3	7.7
9	Typic Hydruudands	Olaa	0-20	SC	5.2	14.1%	53	380	14%	93	22	12	1.8	18.6	37.8	1.3	1.4	28.0	10.6	6.8
10	Typic Hydruudands	Olaa	0-20	SC	5.8	12.4%	19	150	13%	68	17	9.3	1.8	17.6	37.3	1.2	0.9	32.8	8.5	9.8
11	Acrodoxic Hydruudands	Hilo	0-20	SC	6.0	9.1%	5.2	130	4.1%	145	5.7	26	0.2	37.0	121	4.3	2.7	27.8	13.3	6.9
12	Typic Hydruudands	Olaa	0-20	SC	5.6	12.5%	17	190	9.0%	98	20	13	1.5	20.6	43.3	1.4	0.8	33.6	12.8	9.4
13	Typic Hydruudands	Panaewa	0-20	SC	5.6	12.3%	18	120	15%	81	33	10	3.4	9.3	21.7	0.8	0.8	17.5	6.2	6.2
14	Typic Hydruudands	Olaa	0-20	SC	5.2	10.5%	28	270	11%	94	23	11	2.1	16.4	33.3	1.2	0.7	29.9	11.7	9.3
15	Lithic Hydruudands	Panaewa	0-20	SC	5.5	12.2%	26	340	7.6%	100	23	13	1.8	20.3	40.5	1.2	0.6	29.0	11.4	8.1
16	Typic Hydruudands	Olaa	0-20	SC	5.4	14.4%	11	120	9.1%	97	16	13	1.2	26.6	62.1	1.6	0.8			
17	Typic Hydruudands	Waiakea	0-20	SC	5.5	9.8%	13	260	4.9%	123	15	18	0.8	26.1	65.6	1.8	0.9	34.0	13.9	9.7
18	Typic Hydruudands	Waiakea	0-20	SC	5.5	9.5%	20	230	8.6%	95	25	13	1.9	18.6	38.3	1.2	0.5	37.4	12.0	11.6
19	Typic Uqifolists	Papai	0-20	SC	5.4	11.1%	56	160	36%	62	43	7.9	5.4	8.1	9.9	0.2	3.1	15.9	3.6	2.7
20	Lithic Hydruudands	Panaewa	0-20	SC	5.5	15.0%	7.4	65	11%	99	20	13	1.5	18.1	36.4	1.4	0.9	29.2	9.1	8.3
21	Typic Hydruudands	Olaa	0-20	SC	5.3	20.5%	23	410	5.6%	100	20	14	1.5	24.0	46.6	1.2	0.9			
22	Acrodoxic Hydruudands	Ohia	0-20	SC	5.5	10.8%	18	340	5.3%	112	21	17	1.2	25.5	61.4	1.7	1.0			
23	Acrodoxic Hydruudands	Ohia	0-20	SC	5.5	14.7%	8.8	240	3.7%	121	12	20	0.6	31.7	75.5	1.9	1.3			
24	Acrodoxic Hydruudands	Hilo	0-20	SC	6.0	6.8%	3.6	44	8.1%	147	7.1	25	0.3	33.7	107	3.8	0.7			
25	Typic Hydruudands	Panaewa	0-20	SC	6.4	9.9%	29	280	10%	84	34	11	3.2	9.5	33.2	1.2	1.3	15.5	8.1	5.3
26	Typic Hydruudands	Panaewa	0-20	SC	6.5	9.8%	39	300	13%	78	37	9.3	4.0	8.4	23.6	1.2	1.1	17.0	5.9	6.6
27	Typic Hydruudands	Panaewa	0-20	SC	6.7	10.6%	80	490	16%	80	29	10	2.9	10.8	33.5	1.3	1.3	14.8	7.4	5.1
28	Typic Hydruudands	Panaewa	0-20	SC	6.2	13.0%	180	910	20%	88	26	11	2.4	15.1	45.7	1.1	4.5	19.1	9.0	5.4
29	Typic Hydruudands	Panaewa	10	SC	5.6	11.9%	29	400	7.2%	89	28	12	2.3	14.4	30.9	1.2	0.6	29.9	11.4	8.8
30	Typic Hydruudands	Panaewa	20	SC	5.7	9.5%	28	330	8.7%	97	28	13	2.1	15.5	37.6	1.6	0.7	31.5	11.9	9.3
31	Typic Hydruudands	Panaewa	30	SC	5.7	9.7%	24	660	3.7%	107	25	13	1.9	16.9	49.4	2.0	0.6	33.9	14.9	9.7
32	Typic Hydruudands	Panaewa	40	SC	5.8	7.2%	14	330	4.3%	103	28	13	2.3	14.4	45.0	1.9	0.4	36.2	13.9	11.9
33	Typic Hydruudands	Panaewa	50	SC	5.9	7.0%	7.7	180	4.3%	106	28	13	2.2	15.2	46.0	1.8	0.4	38.2	9.9	12.0
34	Typic Hydruudands	Panaewa	60	SC	5.7	9.4%	18	440	4.2%	109	23	13	1.7	18.9	53.4	2.0	0.7	38.2	14.7	11.1
35	Typic Hydruudands	Panaewa	80	SC	5.6	8.2%	5.6	95	5.9%	94	28	12	2.3	14.5	33.4	1.4	0.3	44.9	9.1	13.8
36	Typic Hydruudands	Panaewa	100	SC	6.3	5.5%	1.0	32	3.1%	70	33	8.6	3.8					48.0	5.0	15.6
37	Typic Hydruudands	Panaewa	120	SC	6.2	4.0%	0.6	21	2.8%	62	35	7.9	4.4	6.4	9.2	1.6	0.1	45.6	3.3	16.4
38	Typic Hydruudands	Olaa	0-20	SC	5.7	13.6%	7.8	110	7.2%	110	20	16	1.3	22.9	62.4	2.2	0.9			
39	Lithic Hydruudands	Panaewa	0-20	SC	5.8	18.0%	11	150	7.5%	96	27	14	2.0	20.6	44.9	1.7	0.8			
40	Acrodoxic Hydruudands	Hilo	0-20	SC	5.6	16.6%	3.7	210	1.7%	132	9.4	23	0.4	37.9	98.7	2.7	1.8			
41	Lithic Hydruudands	Panaewa	0-20	SC	5.6	14.9%	13	390	3.2%	143	8.3	23	0.4	28.2	79.3	1.5	0.8			
42	Lithic Hydruudands	Panaewa	0-20	SC	5.7	17.9%	5.6	190	2.9%	118	14	18	0.8	30.2	67.3	2.0	0.9			

Table 2.3 (cont.) Soil Properties, <0.25mm fraction, air-dried basis

Sample ID	Taxonomy	Series	Depth ^a (cm)	Site Use ^b	pH ^c	TOC ^d (wt%)	As _{BAC} ^e (mg kg ⁻¹)	As _{TOT} ^f (mg kg ⁻¹)	As _{BAC} ^g (%)	Fe _{TOT} ^h (mg g ⁻¹)	Ca _{TOT} ⁱ (mg g ⁻¹)	Ti _{TOT} ^j (mg g ⁻¹)	Ca/Ti ^k Ratio	Al _{CD} ^l (mg g ⁻¹)	Fe _{CD} ^m (mg g ⁻¹)	Si _{CD} ⁿ (mg g ⁻¹)	P _{CD} ^o (mg g ⁻¹)	Al _{HAH} ^p (mg g ⁻¹)	Fe _{HAH} ^q (mg g ⁻¹)	Si _{HAH} ^r (mg g ⁻¹)
43	Acrodoxic Hydruandands	Hilo	0-20	CR Site 1	7.2	6.7%	0.7	46	1.5%	121	24	22	1.1	22.2	84.3	6.8	1.1	16.8	13.2	8.4
44	Acrodoxic Hydruandands	Hilo	0-20	CR Site 1	6.9	9.2%	7.3	220	3.4%	113	29	20	1.4	16.1	66.1	4.4	1.4	12.3	9.7	6.1
45	Acrodoxic Hydruandands	Hilo	0-20	CR Site 1	6.1	10.0%	8.8	380	2.3%	102	17	22	0.8	22.3	84.8	2.4	1.4	16.4	11.5	5.1
46	Acrodoxic Hydruandands	Hilo	0-20	CR Site 1	5.9	9.3%	5.1	820	6.2%	104	20	19	1.1	12.0	53.8	2.0	1.3	11.8	7.7	4.4
47	Acrodoxic Hydruandands	Hilo	0-20	CR Site 1	5.8	8.7%	150	2300	6.7%	115	22	21	1.1	20.1	76.7	1.9	1.9	17.2	11.7	4.9
48	Acrodoxic Hydruandands	Hilo	0-20	CR Site 1	5.5	9.9%	1400	9600	15%	129	14	23	0.6	23.6	97.2	2.0	3.2	14.6	12.3	3.2
49	Acrodoxic Hydruandands	Hilo	0-20	CR Site 1	6.1	5.2%	6900	19000	37%	104	27	19	1.5	20.2	81.1	2.6	12.0	11.5	10.6	2.7
50	Acrodoxic Hydruandands	Hilo	80	CR Site 1	7.0	3.2%	6000	25000	24%	125	17	19	0.9	25.6	99.5	2.2	1.8	16.2	4.6	5.2
51	Acrodoxic Hydruandands	Hilo	100	CR Site 1	7.4	3.4%	2400	14000	17%	126	16	21	0.8	24.4	93.7	2.7	1.2	22.5	5.1	7.6
52	Acrodoxic Hydruandands	Hilo	120	CR Site 1	7.5	3.4%	23	2100	1.1%	144	8.2	24	0.3	27.6	101	3.1	0.8	29.3	8.3	8.9
53	Acrodoxic Hydruandands	Hilo	140	CR Site 1	7.4	2.8%	3.0	300	1.0%	141	6.2	24	0.3	31.0	110	3.8	0.9	26.9	9.6	9.2
54	Acrodoxic Hydruandands	Hilo	160	CR Site 1	7.3	2.7%	170	5600	3.1%	161	11	27	0.4	37.3	139	4.3	1.4	17.5	7.2	6.4
55	Lithic Udifolists	Ophikao	0-20	CR Site 2	5.6	14.8%	230	1300	18%	74	38	12	3.3	9.5	26.3	1.5	0.5	15.7	6.2	4.4
56	Lithic Udifolists	Ophikao	0-20	CR Site 2	6.1	13.7%	70	460	15%	77	41	12	3.6	7.6	23.2	1.2	0.5	10.2	4.9	3.3
57	Lithic Udifolists	Ophikao	0-20	CR Site 2	6.5	10.1%	13	250	5.0%	84	40	14	2.9	9.6	34.8	1.8	0.6	12.3	6.6	4.5
58	Lithic Udifolists	Ophikao	0-20	CR Site 2	6.0	28.9%	18	120	16%	52	49	8.1	6.0	3.7	12.1	1.1	0.6	4.7	3.7	1.8
59	Lithic Udifolists	Ophikao	0-20	CR Site 2	6.3	7.2%	2.2	110	2.1%	137	20	40	0.5	15.4	76.6	3.4	1.6	9.4	9.3	3.2
60	Lithic Udifolists	Ophikao	0-20	CR Site 2	5.7	6.2%	<1	61	0.4%	157	60	55	0.1	21.3	109	4.6	2.4	8.8	10.0	2.2
61	Lithic Udifolists	Ophikao	0-20	CR Site 2	5.6	7.9%	0.9	68	1.4%	133	14	34	0.4	19.7	83.2	3.6	1.5	13.4	10.8	3.5
62	Lithic Udifolists	Ophikao	0-20	CR Site 3	7.1	1.8%	140	300	47%	76	54	11	4.7	2.3	12.2	1.3	0.2			
63	Lithic Udifolists	Ophikao	0-20	CR Site 3	6.9	2.6%	260	690	37%	92	47	14	3.3	3.2	21.8	1.2	0.3			
64	Lithic Udifolists	Ophikao	0-20	CR Site 3	7.1	2.0%	220	430	52%	77	55	10	5.3	1.9	15.8	0.7	0.2			
65	Humic Haplustands	Naalehu	0-20	CR Site 4	6.2	3.8%	640	2400	27%	82	31	13	2.4	6.4	41.5	4.8	1.3	7.8	9.4	3.3
66	Humic Haplustands	Naalehu	0-20	CR Site 4	6.4	4.3%	3.1	20	16%	79	35	12	2.9	6.4	36.6	4.4	1.5	8.6	9.1	3.7
67	Humic Haplustands	Naalehu	0-20	CR Site 4	6.4	4.0%	2.4	30	8.2%	84	35	14	2.6	6.6	41.1	5.2	1.5	8.2	9.2	3.3
68	Humic Haplustands	Naalehu	0-20	CR Site 4	6.1	4.7%	1.1	19	5.8%	58	25	9.4	2.7	6.8	33.2	3.4	0.9	9.9	9.6	4.1
69	Humic Haplustands	Naalehu	0-20	CR Site 4	6.2	3.4%	8.8	120	7.1%	84	33	13	2.5	5.6	39.7	4.9	1.2	6.4	8.5	3.1
70	Humic Haplustands	Naalehu	0-20	CR Site 4	6.4	4.3%	2.8	39	7.1%	81	36	13	2.8	6.1	35.3	4.0	1.0	8.5	9.8	3.9
71	Humic Haplustands	Naalehu	0-20	CR Site 4	6.4	3.4%	1.1	70	16%	77	41	12	3.5	3.7	24.9	2.9	1.0	5.7	6.8	2.9
72	Humic Haplustands	Naalehu	0-20	CR Site 4	6.5	2.9%	6.3	51	13%	83	39	13	3.0	4.9	34.1	4.2	1.0	6.2	7.2	2.8

Summary Statistics, Sugar Cane Soils, Ap horizon (0-20 cm depth)

N	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32
Min	5.2	6.8%	0.7	36	1.6%	62	5.7	7.9	0.2	8.1	9.9	0.2	0.5	14.8	3.6	2.7	0.5	14.8	3.6	2.7
Max	7.5	28.9%	6900	25000	52%	171	55	55	6.0	39	159	7.7	12	48	23.4	16.4	4.5	37.4	19.4	11.6
Mean	6.0	9%	280	1300	10%	104	24	17	1.9	18	58	2.4	1.3	22	10	7	1.1	27	11	8
Stdev	0.3	3%	34	170	7%	23	9	5	1.2	9	29	1.0	0.8	7	3	2	0.8	7	3	2

Summary Statistics, All Samples

N	72	72	70	72	72	72	72	72	72	72	72	72	72	71	71	71	71	59	59	59
Min	5.2	1.8%	1	16	0.4%	52	1.2	7.9	0.04	1.9	9.2	0.2	0.1	4.7	3.3	1.8	0.1	4.7	3.3	1.8
Max	7.5	28.9%	6900	25000	52%	171	55	55	6.0	39	159	7.7	12	48	23.4	16.4	4.5	37.4	19.4	11.6
Mean	6.0	9%	280	1300	10%	104	24	17	1.9	18	58	2.4	1.3	22	10	7	1.1	27	11	8
Stdev	0.6	5%	1100	4100	11%	27	12	8	1.4	10	34	1.5	1.5	12	4	3	1.5	12	4	3

Table 2.3 (cont.) Soil Properties, <0.25mm fraction, air-dried basis

Notes and QA/QC Summary

^a Depth of sample, 0-20 cm indicates composite surface soil, discrete depth (i.e. 30 cm) indicates composite sample from excavation pit sidewall

^b Site Use key: SC = Former sugar cane cultivation, CR = Chemical release site

^c Stdev of replicate analyses is 0.10 pH units

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

^e Analysis of As_{BAC} by SBRC-g. Replicate measurements of NIST 2710 control soil indicate CV of 9%.

^f Analysis of As_{TOT} by acid digestion and ICPMS. Replicate measurements of NIST 2710 control soil indicate CV of 6%.

^g As_{BAC} is the As_{BAC} in concentration form divided by As_{TOT}

^h Total Fe analysis by EDXRF, CV of replicate analyses is 2%.

ⁱ Total Ca analysis by EDXRF, CV of replicate analyses is 7%.

^j Total Ti analysis by EDXRF, CV of replicate analyses is 3%.

^k Ca/Ti error (CV) propagated from Ca and Ti replicate analyses is 8%.

^l Citrate-dithionite extract analyzed for Al by ICPOES, CV of replicate analyses is 1.7%.

^m Citrate-dithionite extract analyzed for Fe by ICPOES, CV of replicate analyses is 1.2%.

ⁿ Citrate-dithionite extract analyzed for Si by ICPOES, CV of replicate analyses is 2%.

^o Citrate-dithionite extract analyzed for P by ICPOES, CV of replicate analyses is 8%.

^p Hydroxylamine hydrochloride extract analyzed for Al by ICPOES, CV of replicate analyses is 4%.

^p Hydroxylamine hydrochloride extract analyzed for Fe by ICPOES, CV of replicate analyses is 7%.

^p Hydroxylamine hydrochloride extract analyzed for Si by ICPOES, CV of replicate analyses is 5%.

Table 2.4 Linear Regressions to Predict Bioaccessible Arsenic

1-variable models, $As_{TOT} < 1000 \text{ mg kg}^{-1}$

Dependent Variable	Independent Variables											
	As_{BAC}	pH	TOC	As_{TOT}	Fe_{TOT}	Al_{CD}	Fe_{CD}	Si_{CD}	P_{CD}	Al_{HAH}	Fe_{HAH}	Si_{HAH}
N		63	63	63	63	62	62	62	62	50	50	50
Correlation			(+)	(+)	(-)	(-)	(-)	(-)				
R^2		<0.01	0.05	0.67	0.18	0.16	0.31	0.55	<0.01	<0.01	<0.01	<0.01

1-variable regression equations², $As_{TOT} < 1000 \text{ mg kg}^{-1}$

$$\log As_{BAC} = (1.31 \times \log As_{TOT}) - 1.88$$

2-variable models, As_{TOT} plus a 2nd variable, $As_{TOT} < 1000 \text{ mg kg}^{-1}$

Dependent Variable	Independent Variables											
	As_{BAC}	As_{TOT}	pH	TOC	Fe_{TOT}	Al_{CD}	Fe_{CD}	Si_{CD}	P_{CD}	Al_{HAH}	Fe_{HAH}	Si_{HAH}
N			63	63	63	62	62	62	62	50	50	50
Correlation		(+)	(+)		(-)	(-)	(-)	(-)		(-)	(-)	(-)
R^2			0.68	0.67	0.85	0.83	0.86	0.78	0.67	0.71	0.76	0.71

2-variable regression equations, $As_{TOT} < 1000 \text{ mg kg}^{-1}$

$$\log As_{BAC} = (1.29 \times \log As_{TOT}) - (2.54 \times \log Fe_{TOT}) + 3.21$$

$$\log As_{BAC} = (1.30 \times \log As_{TOT}) - (0.90 \times \log Al_{CD}) - 0.82$$

$$\log As_{BAC} = (1.19 \times \log As_{TOT}) - (1.14 \times \log Fe_{CD}) + 0.26$$

2-variable regression equations, all samples (N=72)

$$\log As_{BAC} = (1.30 \times \log As_{TOT}) - (2.64 \times \log Fe_{TOT}) + 3.39, R^2 = 0.91$$

$$\log As_{BAC} = (1.29 \times \log As_{TOT}) - (0.94 \times \log Al_{CD}) - 0.75, R^2 = 0.90$$

$$\log As_{BAC} = (1.30 \times \log As_{TOT}) - (1.12 \times \log Fe_{CD}) - 0.02, R^2 = 0.91$$

Notes:

All variables expressed in \log_{10} concentration form, except pH

Concentrations in following units: As_{BAC} and As_{TOT} in mg kg^{-1} ; Fe_{TOT} , Al_{CD} , Fe_{CD} in mg g^{-1}

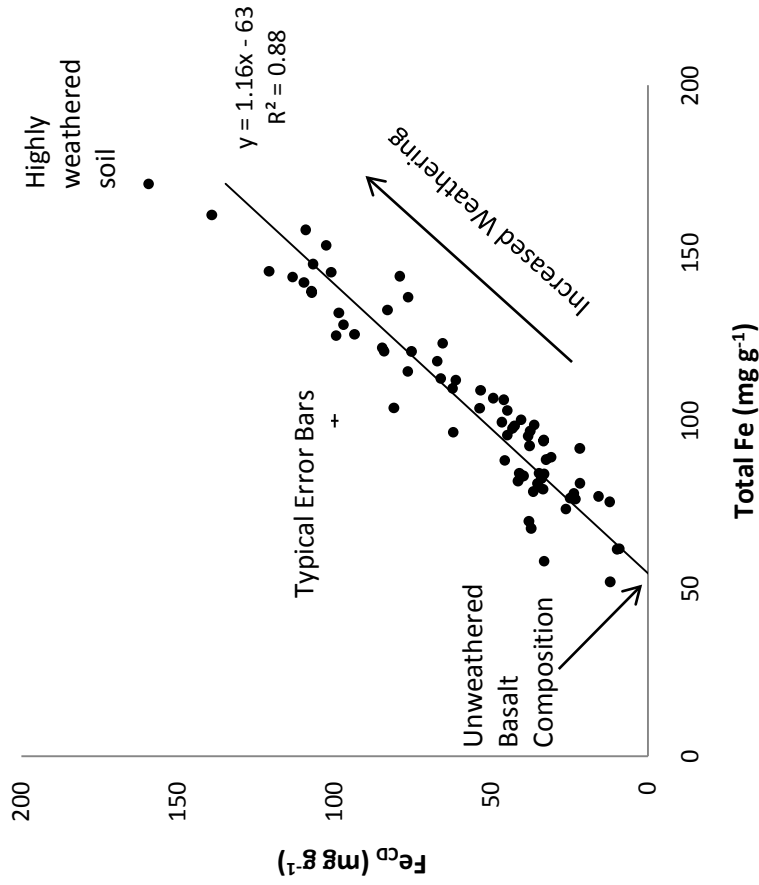


Figure 2.1 Cross-plot of total Fe versus citrate-dithionite extractable Fe (Fe_{CD}). Measurement uncertainties (CV) are shown by “typical error bars” at 2% for Fe_{TOT} and 1.2% for Fe_{CD}, based on replicate analyses. Unweathered basalt, with Fe in igneous mineral phases, has little or no Fe_{CD}, indicating no formation of pedogenic Fe phases. Weathering increases pedogenic Fe over igneous Fe phases, and in highly weathered soils (Acruoxic Hydrudands) nearly all Fe is in pedogenic phases.

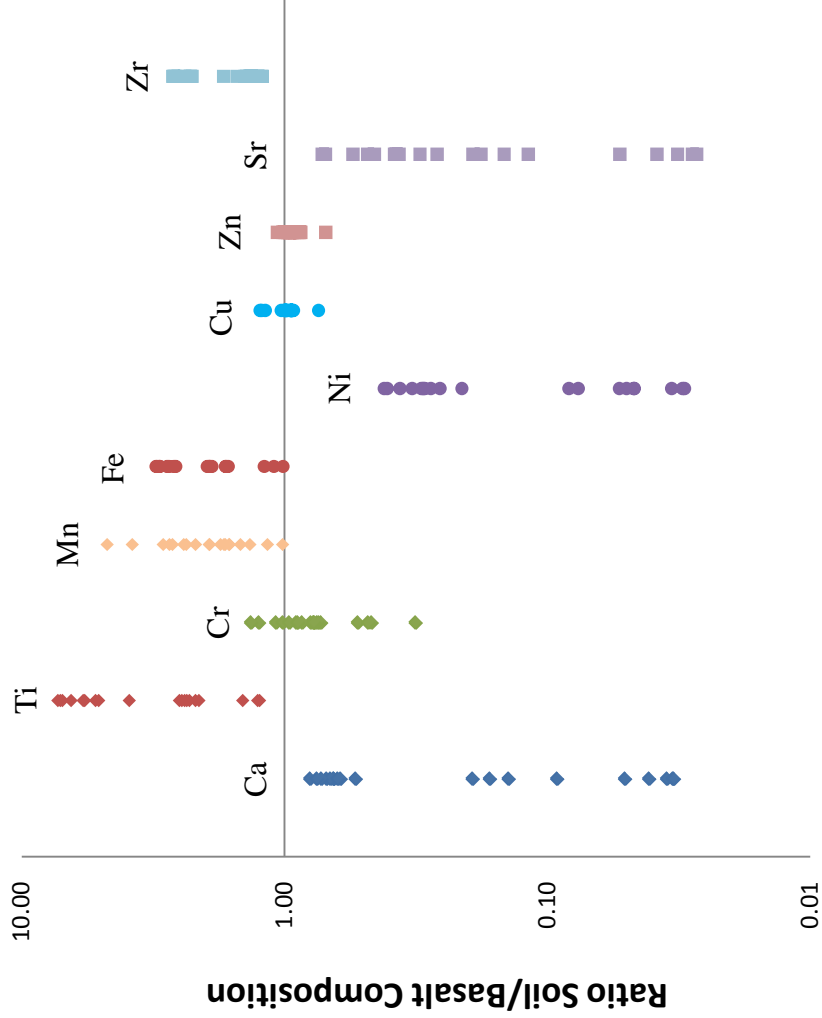


Figure 2.2 Major and trace elements in soils compared to parent Kau Basalt composition (from Wolfe and Morris, 1996). Soil elemental analysis by EDXRF on <0.25 mm fraction, adjusted to mineral-phase basis by loss on ignition (LOI). Note strong accumulation of Ti, Mn, Fe and Zr; with depletion of Ca, Ni, and Sr. Weathering trends are well defined by a ratio of accumulating/depleting elements, i.e. Ca/Ti or Sr/Zr.

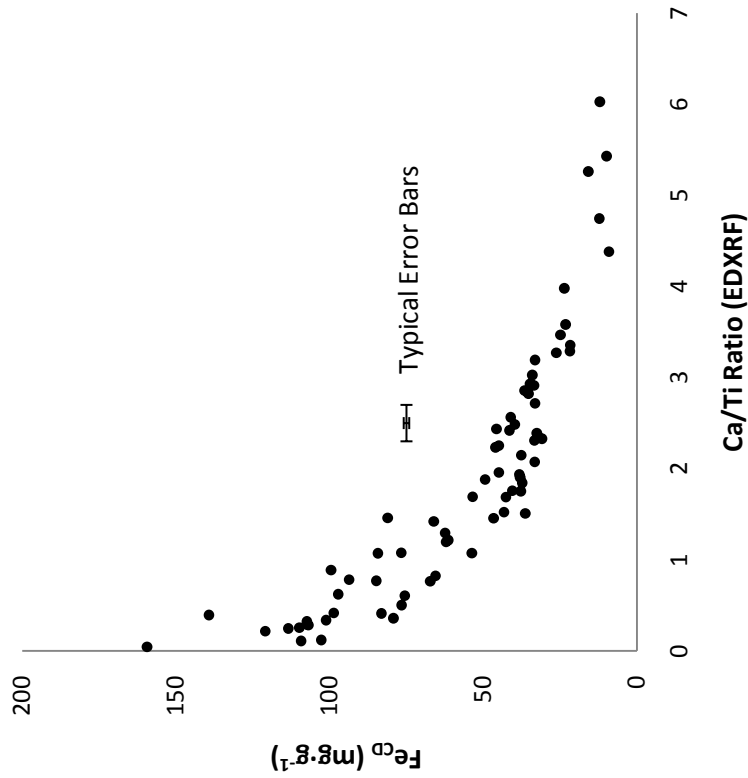


Figure 2.3 Cross-plot of Ca/Ti ratio to citrate-dithionite extractable Fe, EDXRF analysis of <0.25 mm soil fraction. Increase in reactive Fe (Fe_{CD}) is coincident with reduction in Ca/Ti ratio, indicating soil weathering and development of pedogenic solid phases. Typical error bars indicate relative error (CV) of 1.2% for Fe_{CD} and 8% for Ca/Ti ratio.

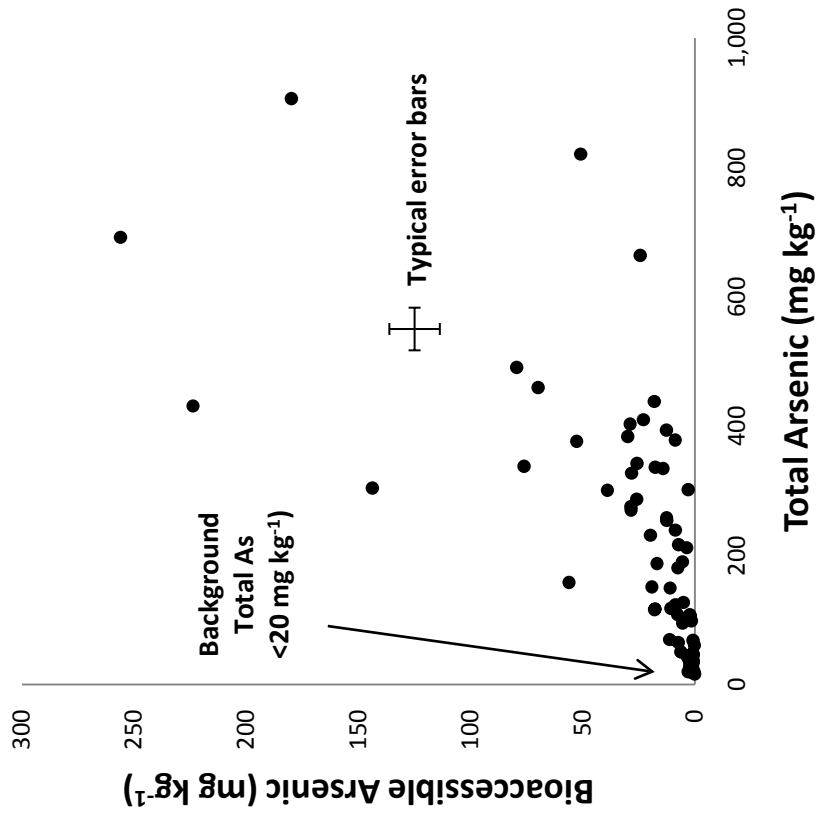


Figure 2.4 Cross-plot of total arsenic and bioaccessible arsenic. Note the wide variation in As_{BAC} , especially at higher As_{TOT} loadings. Based on replicate analyses of NIST 2710 control soil, relative error (coefficient of variation) is 6% for As_{TOT} and 9% for As_{BAC} , as shown by “typical error” bars.

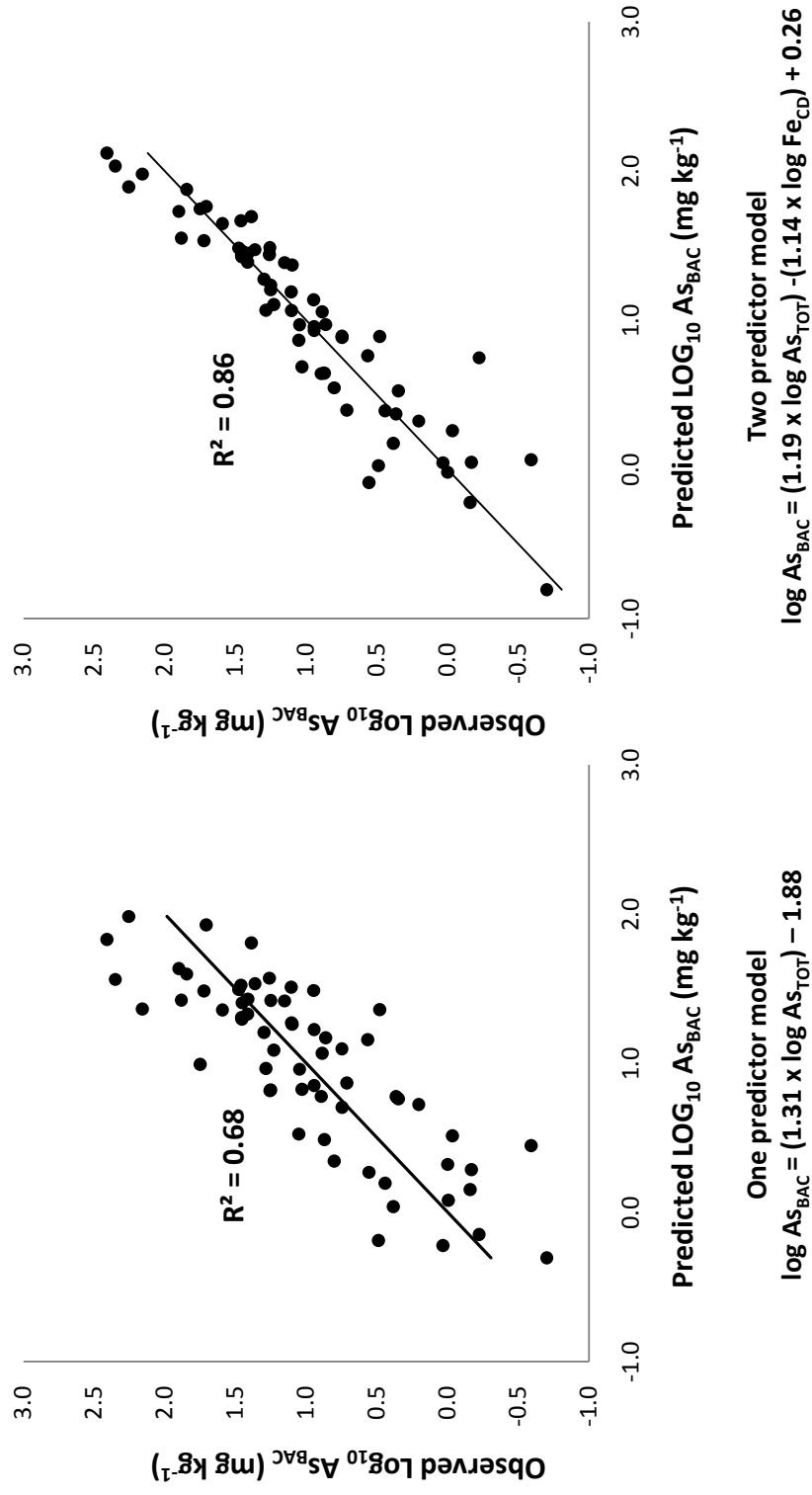


Figure 2.5 Predictions of bioaccessible arsenic from total arsenic and citrate-dithionite extractable Fe. A single predictor model using As_{TOT} results in correlation coefficient (R^2) of 0.68. Adding a second predictor variable, consisting of a key soil property (Fe_{TOT} , Fe_{CD} or Al_{CD}) greatly improves prediction (R^2 of 0.85-0.86).

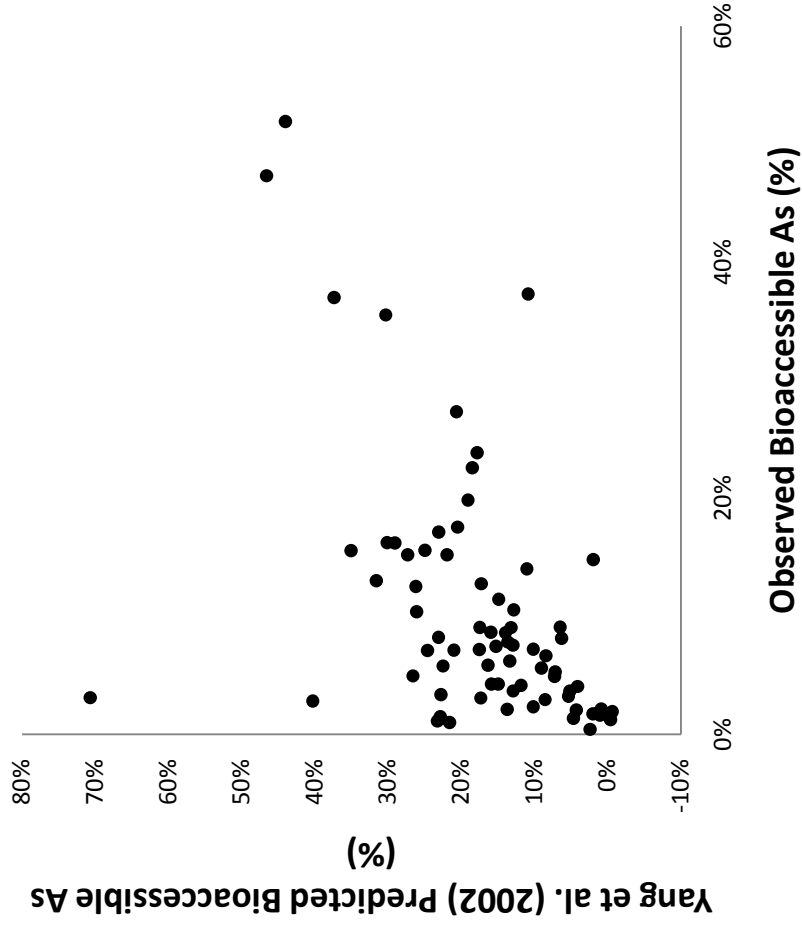


Figure 2.6 Observed percentage of bioaccessible As ($As_{BAC\%}$) from current study soils, compared to predicted $As_{BAC\%}$ based on Yang et al. (2002) regression equation for suite of U.S. soils. Yang et al. (2002) model does not accurately predict $As_{BAC\%}$, especially for values less than 20% (most soils in study area).

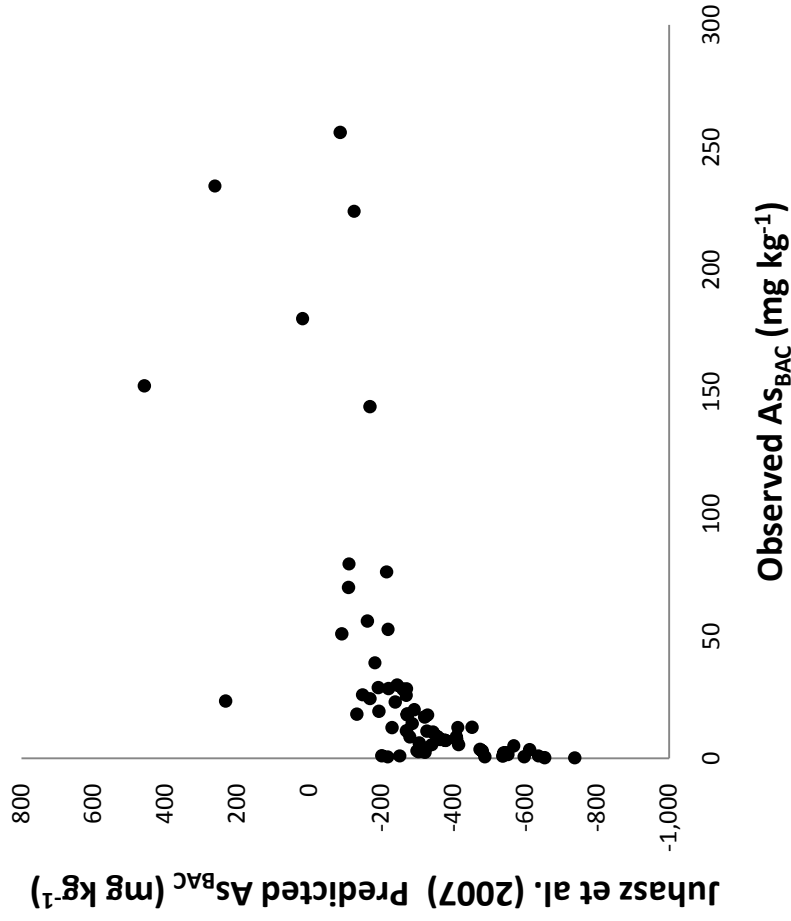


Figure 2.7 Observed bioaccessible As (concentration basis) from study soils, compared to predicted bioaccessible As using Juhasz et al. (2007) regression equation. Juhasz model predicts significantly lower As_{BAC} than observed, especially at lower concentrations.

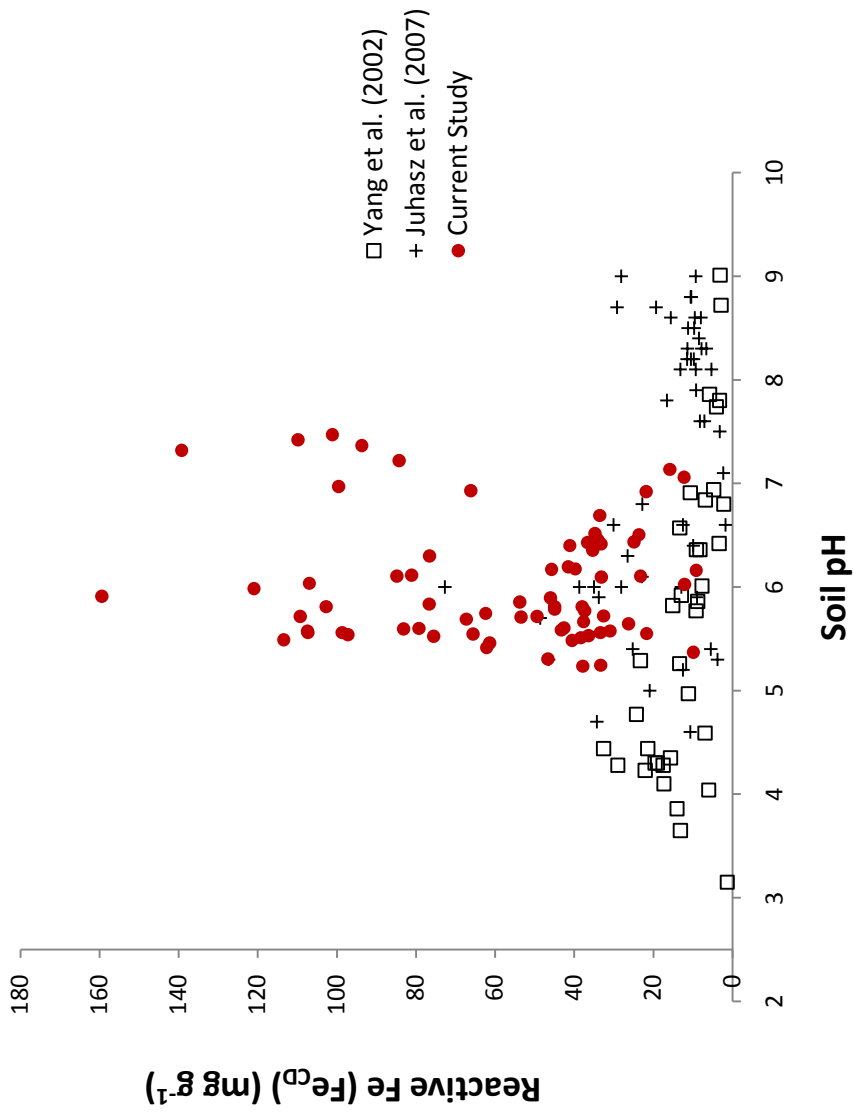


Figure 2.8 Comparison of key soil properties, pH and reactive Fe (Fe_{CD}) from soil suites modeled by Yang (2002), Juhasz (2007a) and current study. Hawaiian Andisols show narrow pH range, but large range of Fe_{CD} . Predicting AS_{BAC} in Fe-rich Hawaiian soils is best accomplished using a soil-specific model, as opposed to a model developed for dissimilar soils.

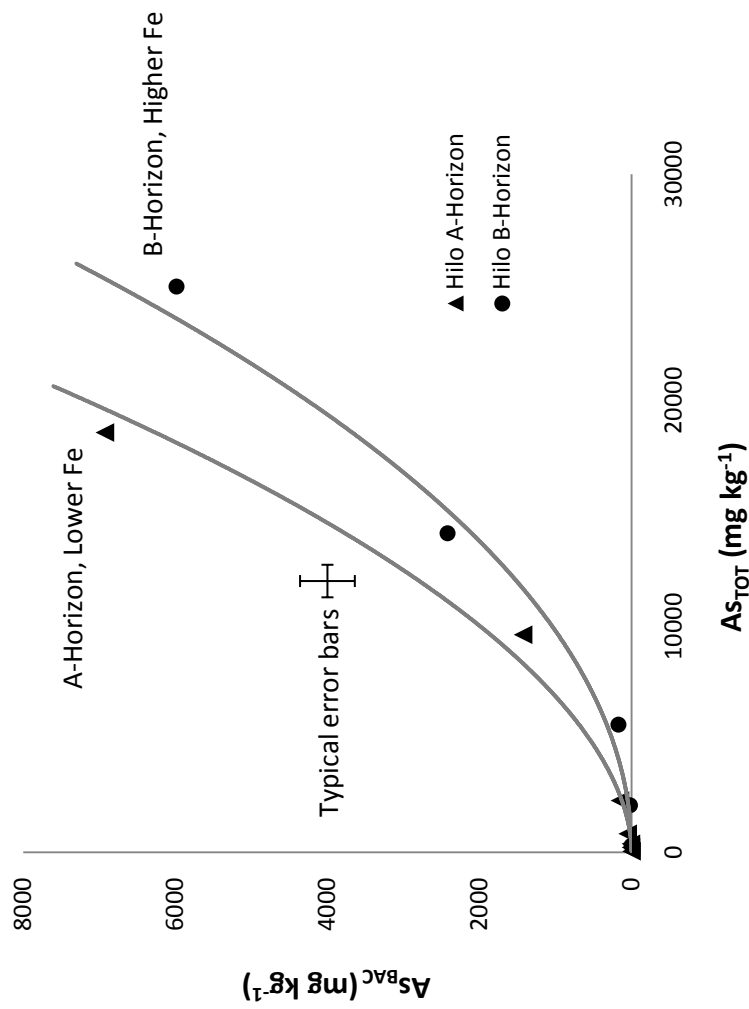


Figure 2.9 Cross-plot of total versus bioaccessible As for soils at a chemical release site. Percentage of As_{BAC} increases more than ten-fold across range As_{TOT} observed (46 to 19,000 $mg\ kg^{-1}$ for A-horizon). Soils with higher Fe content show lower As_{BAC} at similar As_{TOT} loadings. Error bars show relative error (CV) based on replicate analyses of NIST SRM 2710, 6% for As_{TOT} and 9% for As_{BAC} .

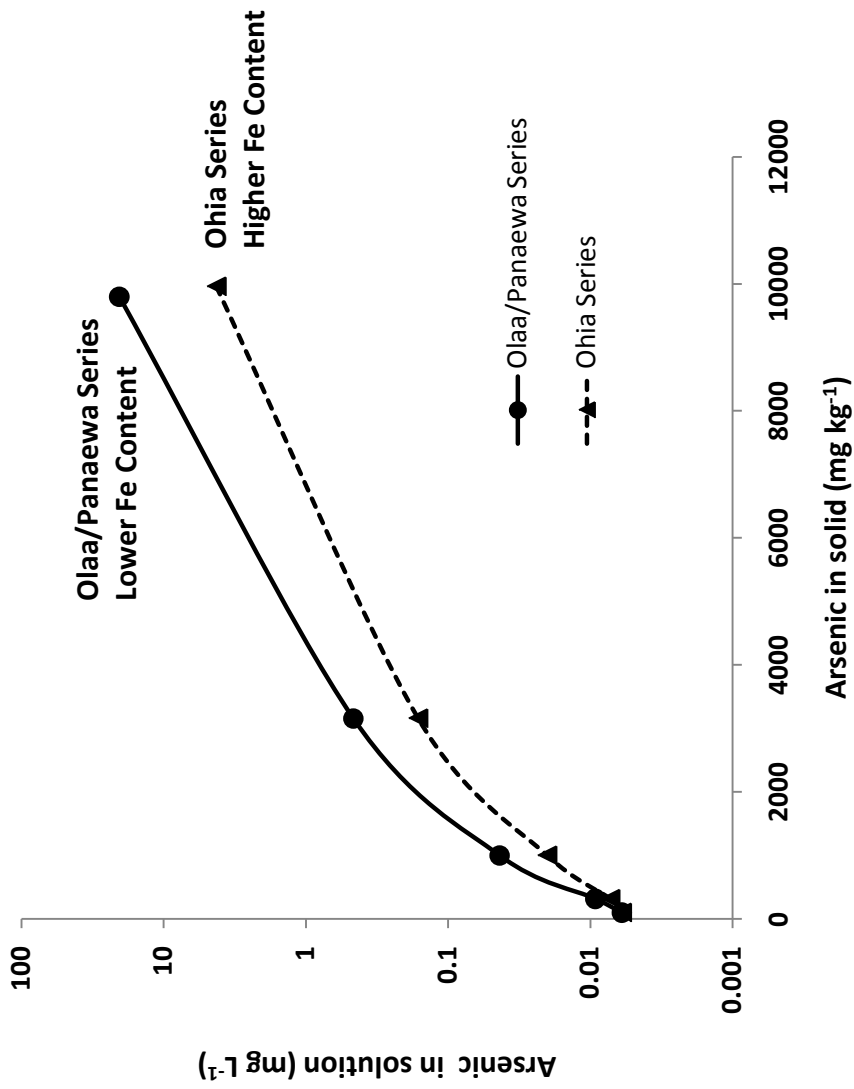


Figure 2.10 Arsenate equilibrium sorption isotherms for a lower Fe-content soil (Typic Hydrudands, Fe_{CD} of 35 $mg\ g^{-1}$) and higher Fe-content soil (Acrodoxic Hydrudands, Fe_{CD} of 120 $mg\ g^{-1}$). Increased As sorption capacity of higher Fe soils coincides with lower observed As_{BAC} (at similar As_{TOT} loadings).

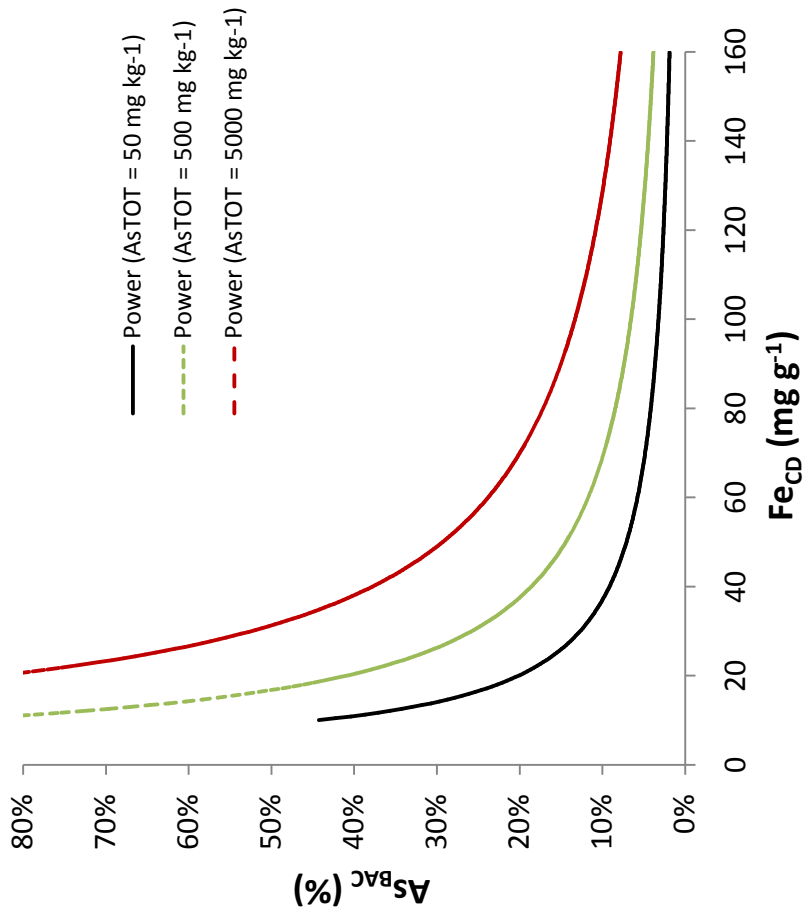


Figure 2.11 A class of curves with fixed As_{TOT} , developed from the 2-predictor variable regression model (Equation 4), showing predicted changes in $As_{BAC\%}$ based on variable reactive Fe (Fe_{CD}) content. Note that $As_{BAC\%}$ increases dramatically in soils containing less than 50 mg g⁻¹ Fe_{CD} . Study soils ranged from 9.2 to 159 mg g⁻¹ Fe_{CD} , averaging 58 mg g⁻¹ (see Table 2.3).

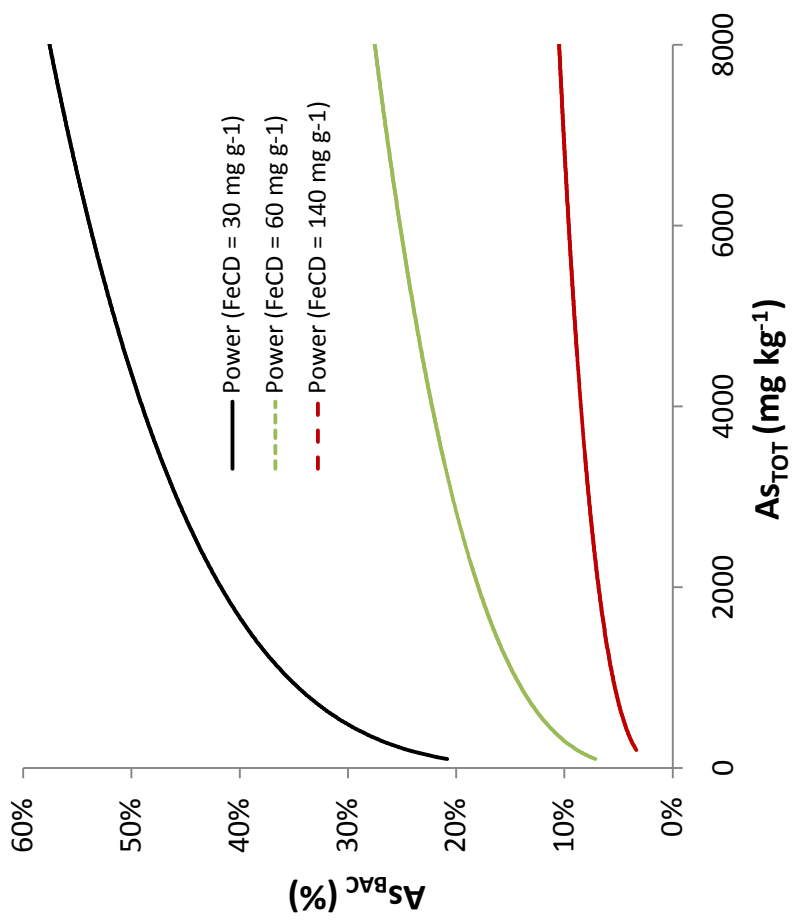


Figure 2.12 A class of curves with fixed Fe_{CD} content, developed from the 2-predictor variable regression model (Equation 4), showing predicted changes in $As_{BAC\%}$ based on variable As loading (As_{TOT}) content. Note that $As_{BAC\%}$ increases more substantially with increasing As_{TOT} in soils containing lower levels of reactive Fe (Fe_{CD}).

Chapter 3. Iron Amendments to Reduce Bioaccessible Arsenic

Abstract

Former sugar cane lands on the Big Island of Hawaii have elevated soil arsenic (As) from historical use of arsenical pesticides. The bioaccessible fraction of total As (As_{TOT}) is a measure of the potential for human As uptake by incidental ingestion of soil, and is used in the assessment of human health risk and the need for remedial action. Ferric chloride plus lime and ferrous sulfate plus lime were applied to As-contaminated soils in a field plot setting to determine the potential for reducing bioaccessible As (As_{BAC}) by formation of additional iron (Fe) oxyhydroxide substrate. The two Fe sources performed similarly in reducing As_{BAC} over the 1-2 year observation period, with 30-41% reduction in As_{BAC} for 0.25 wt % Fe dosing (dry soil basis) and 59-63% reduction for 0.5 wt % Fe dosing. Addition of phosphate to treated and untreated soils caused a significant increase in As_{BAC} . Fe-treated and control soils showed more than a doubling of As_{BAC} after addition of 1500 mg P kg⁻¹ to the <2 mm soil fraction. The cost of in-situ treatment of As-contaminated soil with ferrous sulfate plus lime to lower As_{BAC} is estimated to be an order of magnitude less than excavation and landfill disposal on the Island of Hawaii, making the technology a viable remedial alternative when remedial action objectives are based on As_{BAC} levels.

3.1 Introduction

Problem Definition, Objectives

At many locations within the Hawaiian Islands, arsenic (As) has been identified in soils at concentrations significantly above naturally-occurring background levels (<20 mg kg⁻¹; USDA-NRCS, 2011). Arsenic soil contamination is predominantly the result of historic spray application of inorganic As herbicides on sugar cane lands, and release of As at herbicide storage and mixing areas. Extensive areas of former sugar cane cultivation on the Island of Hawaii show soil As concentrations from 50 to 1000 mg kg⁻¹ (Chapter 1). Some former pesticide mixing areas have soil As concentrations greater than 20,000 mg kg⁻¹. *In vitro* bioaccessible As (As_{BAC}), a surrogate for human oral relative bioavailability, ranges from less than 1% to more than 50% of total As (As_{TOT}) in Hawaiian soils (Chapters 1 and 2). The Hawaii Department of Health (HDOH) has developed guidance for using the As_{BAC} content of soil (not As_{TOT}) in assessing the potential for human health risk and determining the need for remedial action (HDOH, 2006; 2010). Soils with As_{BAC} concentrations exceeding 23 mg kg⁻¹ typically require mitigation in an unrestricted land use setting (HDOH, 2010).

Most soils on the Island of Hawaii are Andisols, young soils developed from the weathering of volcanic rock and tephra, rich in poorly-crystalline to non-crystalline pedogenic solid phases including iron oxyhydroxides (ferrihydrite and goethite), aluminosilicates (allophane and imogolite), and metal-humus complexes. Andisols

display a strong affinity for inorganic As (arsenite/arsenate) and other oxyanions such as phosphate. Sequestering of As in these pedogenic solid-phase materials, in particular the Fe oxyhydroxide phases, is believed to be the dominant mechanism that results in low bioavailability and bioaccessibility of soil As (Chapter 2). The dominant controls on A_{SBAC} are the degree of As contaminant loading (A_{STOT}) and the quantity of pedogenic substrate consisting of iron (Fe) oxyhydroxide, aluminosilicates and Fe, Al-humus complexes. The concentration of pedogenic substrates can be estimated by citrate-dithionite (CD) extractable Fe or Al; or by total Fe (Fe_{TOT}) content, which is positively correlated with CD-extractable Fe (Fe_{CD}) (Chapter 2).

Despite the strong natural capacity of Hawaiian Andisols to sequester As, some soils with high A_{SBAC} require remedial action. Traditional remedial technologies for As-contaminated soil consist of removal and landfill disposal, or capping with clean soil (or with redevelopment infrastructure such as parking lots or buildings). In situ treatment technologies to remediate soil by reducing A_{SBAC} may prove to be technically robust and cost effective at some As-contaminated sites, especially those with localized areas of higher As-contaminated soils, such as former herbicide storage or mixing areas facilities.

Previous Studies to Reduce Bioaccessible Arsenic

Iron oxyhydroxides strongly sorb oxyanions of As, phosphorus, selenium, molybdenum and others (Roy et al., 1986). Removal of dissolved As from wastewater using ferric iron compounds is a proven technology (USEPA, 2002a). The use of Fe substrates as soil amendments to reduce As mobility and toxicity has been studied at the laboratory and field pilot scale. Sources of Fe have ranged included industrial-grade chemical compounds (e.g. ferrous sulfate), natural minerals (goethite and hematite) and industrial waste by-products (e.g. water treatment sludges, ore processing muds). Goals of soil treatment techniques have included reduction of As mobility (leaching), reduced uptake in crops, and reduced oral bioavailability to humans.

Martin and Ruby (2003) evaluated the reduction in A_{SBAC} (using the physiologically-based extraction test (PBET); Ruby et al., 1996) in lead and As-contaminated soils from a smelter site by addition of various soil amendments. They observed an 84% reduction in A_{SBAC} with the addition of 5 wt % ferrihydrite to the contaminated soil after a 33-week period of wet-dry cycling. Along with the reduction in A_{SBAC} , they observed a 5-fold reduction in leachable As measured by the synthetic precipitation leaching procedure (SPLP; EPA Method 1312). Lombi et al. (2004) evaluated the reduction in A_{SBAC} in soils amended with various industrial waste by-products. Their testing showed statistically significant reductions in A_{SBAC} (by about 25%) in only one of five amendment materials, an Fe-rich wastewater treatment sludge. In another study of industrial by-products as soil amendments, Mench et al. (2006) determined that iron grit could reduce A_{SBAC} (PBET) by 75% over a 6-year long greenhouse plot study. Subacz et al. (2007) evaluated efficacy of different Fe amendments on a suite of nine As-contaminated soils amended in the

laboratory with ferrous chloride, ferric chloride, ferric bromide and zerovalent (metallic) iron, and found that over a 7 to 28 day testing period soluble Fe salts performed better in reducing AS_{BAC} than metallic Fe. On average for the nine soils, $FeCl_3$ amendment at a dosing rate of 100 moles per mole As reduced AS_{BAC} by a factor of two. The authors determined that a soil moisture content of at least 30% was required to facilitate the observed reduction in bioaccessibility, and that lime addition in concert with Fe addition may be necessary to control pH in soils lacking natural buffering capacity.

The current study builds on the prior work just summarized that indicates that Fe amendments may provide significant reductions in AS_{BAC} . To date there is little information on the long-term viability of Fe amendments to reduce AS_{BAC} under field conditions. Our primary goal was to determine whether significant reduction in AS_{BAC} could be achieved and maintained over a period of several years in a garden plot setting using Fe-amendment products readily available in Hawaii (ferric chloride and ferrous sulfate). In addition, the reversibility of reduced As bioaccessibility was explored by application of phosphate, which will compete with As for sorption sites on Fe oxyhydroxides. Addition of phosphate is a realistic scenario if amended soils were used for gardening, landscaping or agricultural purposes, and phosphate-based fertilizers were applied.

3.2 Materials and Methods

Study Soils

The study site is located in the town of Kea'au, Island of Hawaii, on the east flank of the Mauna Loa volcano. The location was formerly in sugar cane cultivation, and arsenical herbicides were applied directly to soils by spray application from about 1915 to 1950 (Hanson, 1959). Soils are Hydudands formed from the weathering of underlying basaltic lava flows and subsequently deposited volcanic ash. These soils formed at an elevation of 100 m above mean sea level with mean annual temperature of 20.5° C and annual rainfall of 4000 mm (HDBEDT, 2011). The age of the underlying lava flow is approximately 5,000 to 11,000 y bp (Wolfe et al., 1996) and a soil profile of approximately 1m thickness has developed. At the field plot location, soils are developed on porous pahoehoe lava, and are very well drained. Andisols are characterized by andic properties in the fine soil fraction, including: low bulk density, high phosphate retention, and significant ammonium oxalate-extractable Al and Fe (USDA-NRCS, 2006). The fine silt and clay fraction (less than 10 μ m) was examined by Cutler (Chapter 1) using transmission electron microscopy. Three dominant pedogenic solid-phase materials were observed in study soils: Fe oxyhydroxides, short-range order aluminosilicates (allophane and imogolite), and metal-humus complexes. Less abundant phases included layered silicates (halloysite, smectite), opaline silica, and partially-weathered volcanic glass. The test plot was located in Ap horizon soils, with total As (AS_{TOT}) of 790 mg kg⁻¹ and AS_{BAC}

of 30 mg kg⁻¹ (4% of A_{STOT}). Soils were slightly acidic (pH 5.6) and had total organic carbon content of 11 wt %. Nearly 50 percent of total Fe content (90 mg g⁻¹) was considered reactive (citrate-dithionite extractable). Basic soil properties are provided in Table 3.1.

Bioaccessible Arsenic Testing

In vitro bioaccessibility assays can be used to estimate relative oral bioavailability of metal(loid)s (Ruby et al., 1996). *In vitro* test methods used to evaluate A_{SBAC} include the PBET, the in-vitro gastrointestinal model (IVG; Rodriguez et al., 1999) 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 extraction at near neutral pH. For this study we have chosen to use the gastric phase of the SBRC test (SBRC-g), which has been correlated with *in vivo* (swine) relative As oral bioavailability for a suite of contaminated soils by Juhasz et al. (2009). In a comparison study of PBET, IVG and SBRC methods for a suite of 20 soils from locations in Kea'au vicinity, within 1 km of the study test plot (HDOH, 2007), the SBRC-g *in vitro* method generated the highest A_{SBAC} values (percentage basis) of all methods (Table 1.2). Use of the SBRC-g method for determining A_{SBAC} in these soils is considered “conservative” relative to other *in vitro* test methods, since it provides the highest estimate of A_{SBAC} and therefore minimizes the potential for a type II error, such as failing to identify a potential health risk when an actual risk is present.

SBRC-g test consisted of extraction of 1 g of <0.25 mm air-dried soil by 100 mL of glycine-buffered HCl at pH 1.5 at 37°C for 1 hour. An aliquot of extraction fluid was filtered through a 0.45 µm cellulose acetate filter and analyzed for As by inductively-coupled plasma (ICP) spectrometry. Quality assurance/quality control procedures included reagent blanks, reagent blank spikes, soil matrix spikes, duplicate sample analyses and standard reference material analyses (Drexler and Brattin, 2007). A second aliquot of soil was evaluated for A_{STOT} using an acid digestion (EPA methods 3050B or 3052) and ICP analysis of the acid extract. The concentration of A_{SBAC} is the mass of dissolved As in the *in vitro* extract divided by the mass of test soil. The percentage of A_{SBAC} is the mass of dissolved As in the *in vitro* extract divided by mass of A_{STOT} in the test soil times 100. In addition to analyzing for As, total soil digests and *in vitro* extracts were also analyzed for Fe (Fe_{TOT} and Fe_{BAC}), in order to evaluate the stability of native and amended Fe substrates in the SBRC-g test..

Laboratory Treatability Testing

Surface soils (0-20cm depth) from a location in the vicinity of the anticipated field plot were evaluated in the laboratory to determine Fe dosing rates for field trials. Soils were air dried and sieved to <2 mm grain size prior to amendment with ferric chloride (FeCl₃) and ferrous sulfate heptahydrate (FeSO₄·7H₂O). Solid iron salts were dissolved in 18

megaohm distilled water and mixed with 100 grams of air dried soil (<2mm fraction) in glass beakers, resulting in moisture content just below field saturation. Amendment solutions were prepared to increase soil Fe content by 0.25, 0.5 and 1 percent on a dry soil weight basis. After adding Fe solutions, powdered hydrated lime ($\text{Ca}(\text{OH})_2$) was added in stoichiometric proportion to iron (1.5 moles lime per mole Fe) to prevent a drop in pH and promote ferric oxyhydroxide precipitation (Subacz et al., 2007). Soils were thoroughly mixed after lime addition, kept moist for 1 week, then air dried and sieved to <0.25 mm for AS_{BAC} analysis.

Field Plot Study

The field test plot consisted of 5 adjacent test cells, each 1.0 m by 0.5 m in dimension. Soils were partially homogenized by hand tilling to a depth of 20 cm across the test plot prior to placing dividers to define and isolate the cells. Stones greater than approximately 5 cm in diameter were hand removed to improve amendment mixing. Four cells were designated for FeCl_3 and FeSO_4 addition, each at two dosing rates, and a fifth cell was left un-amended as a control.

FeCl_3 and FeSO_4 substrates were added at dosing rates of 0.25 and 0.5 wt % Fe per dry soil mass, assuming 20 cm application depth. The dosing rates were selected based on favorable results in laboratory treatability testing. A dosing rate of 1.0 percent Fe was not included, since it was likely to be non-economic in a full-scale application (1 acre or more). FeCl_3 was applied as a solution by spraying, whereas ferrous sulfate heptahydrate was added as a granular solid. Powdered hydrated lime was added to each test plot in proportion to Fe addition, with 1.5 moles lime per mole Fe. A fifth cell was left untreated as a control. After adding Fe substrate and lime, soils were mixed by hand tilling to 20 cm depth. Light grey filter fabric was placed over the soils to inhibit plant growth and prevent excess drying of surface soils. Soils were watered several times a week for the first two weeks after amendment addition, after which natural rainfall was relied upon for moisture control.

Soils from each cell were sampled prior to treatment and at 60, 135, 336 and 612 days post treatment. Sampling was performed using a multi-increment sampling technique (USEPA, 2002b) in which approximately 50 randomly distributed sample increments of approximately 5 grams each were collected from the 0-20 cm depth interval, and homogenized to create a master sample for analysis. Post-treatment soils were air dried and sieved to <0.25 mm prior to SBRC-g testing.

Targeted Extractions, pH and Redox Measurements

Samples collected 336 d post treatment were analyzed for reactive Fe content by the citrate-dithionite (CD) method (Poulton and Canfield, 2005; Raiswell et al., 1994), consisting of extraction of approximately 80 mg of air dried soil in 12 mL of extractant in 15 mL polyethylene centrifuge tubes with continuous shaking over 2 h. Extractant was

composed of 50 g/L sodium dithionite in a pH 4.8 buffer of 0.35 M acetic acid and 0.2 M sodium citrate. At the end of the test duration, tubes were centrifuged for 5 min at 2000 g and supernatant was decanted and filtered through 0.45 μm polypropylene filter. Filtrate was analyzed for Fe by ICP. Poulton and Canfield (2005) showed that the CD extraction provided the most complete dissolution of Fe oxyhydroxide and oxide pedogenic mineral phases, as compared to other common extraction techniques (e.g. hydroxylamine hydrochloride, ammonium oxalate). Soils collected 336 d after treatment were analyzed for pH and oxidation-reduction potential in 1:1 soil:water slurries.

Phosphate Amendments of Fe-treated Soils

For most soil-like materials, the sorption behavior of phosphate (PO_4) and AsO_4 has been shown to be similar (Roy et al., 1986; Manning and Goldberg, 1996). Phosphate has been shown to compete with As for sorption on iron oxyhydroxides (Jackson, 2000; Jain, 2000). Violante and Pigna (2002) evaluated the relative sorption of AsO_4 and PO_4 on selected phyllosilicates, metal oxides, synthetic organo-mineral complexes and soils. They determined that aluminosilicates (including allophane and non-crystalline Al hydroxide) and organo-mineral compounds sorbed PO_4 more strongly than AsO_4 . The opposite was observed for Fe, Mn and Ti oxides and phyllosilicates rich in Fe, which were more effective at sorbing AsO_4 than PO_4 .

To evaluate the permanence of the Fe treatment technology, soils collected 336 d after treatment were amended in the laboratory with PO_4 to evaluate the potential for reversibility of the lowered As bioaccessibility if PO_4 was applied (e.g. phosphate-based fertilizers). Approximately 50 g subsamples of field-moist soils previously treated with 0.5 percent Fe by FeCl_3 and FeSO_4 , along with the control (un-amended) soil, were further amended with a KH_2PO_4 solution at dosing rates of 0, 240, 600 and 1500 mg P kg^{-1} soil (dry-weight equivalent). These P amendment rates span the range of potential phosphate fertilizer additions that may occur in agricultural applications (Hue and Silva, 2000). After P addition, soils were thoroughly mixed and maintained at 23°C and 80% humidity for a period of two weeks. At the end of the 2 week period, soils were air dried and sieved to <0.25 mm in preparation for SBRC-g testing.

X-ray Adsorption Spectroscopy

X-ray adsorption spectroscopy (XAS) was performed on 0.5% FeCl_3 amended and control soils collected 135 d post treatment. Samples were analyzed by X-ray absorption spectroscopy (XAS) at beamline 10-ID (Materials Research Collaborative Access Team) at the Advanced Photon Source at Argonne National Laboratory, Argonne, Illinois. XAS spectra were collected in fluorescence mode using an Ar-filled Lytle detector with a 3 μm thick Z-1 filter to reduce unwanted X-ray fluorescence. The electron storage ring operated at 7 GeV. The light source was equipped with a Si 111 monochromator with the horizontal slit set at 6 mm and the vertical at 2.3 mm.

The collected spectra were analyzed using the Athena and Artemis software programs in the computer package IFEFFIT (Ravel and Newville, 2005). At least three individual spectra were averaged followed by subtraction of the background through the pre-edge region using the Autobk algorithm (Newville et al., 1993). The averaged spectra were normalized to an atomic absorption of one, and the EXAFS signal was extracted from the spectra. The data were converted from energy to photoelectron momentum (k-space) and weighted by k^3 . EXAFS spectra were calculated over a typical k-space range with a Hanning window and 1.0 width Gaussian wings. Fourier transforms (FT) were performed to obtain the radial distribution function (RDF) in R-space. Plotted R-space (\AA) data are not phase shift corrected, the true distances are between 0.3 and 0.5 \AA longer than the distances shown. The spectra were fit with the FEFF8 computer code which uses ab initio calculations to determine phase shift and amplitude functions for single and multiple atomic scattering paths. Crystallographic structures for arsenate pentoxide (As_2O_5), scorodite (FeAsO_4), and alarsite (AlAsO_4) were used to develop theoretical fitting paths.

3.3 RESULTS

Laboratory Treatability Testing

Results of bench-scale testing are provided in Table 3.2. The control soil (un-amended) contained 92 mg kg^{-1} of As_{BAC} (16% of $575 \text{ mg kg}^{-1} \text{As}_{\text{TOT}}$). Reduction in As_{BAC} was consistent with the magnitude of amendment dosing. For soils amended with FeCl_3 and lime, As_{BAC} was reduced 18, 31 and 51 percent, versus control, for 0.25, 0.5 and 1 wt % Fe-equivalent dosing rates. Amendment with FeSO_4 and lime showed a similar trend of As_{BAC} reduction with increasing amendment dosing, however the magnitude of reduction was less than for FeCl_3 . At the highest dosing rate of 1 wt % Fe-equivalent, a 22 percent reduction in As_{BAC} (versus control) was observed, less than half of the reduction observed for FeCl_3 amendment at the same Fe dosing rate. Based on bench-scale findings, both FeCl_3 and FeSO_4 were selected for field trials, at dosing rates of 0.25 and 0.5 wt % Fe to dry soil mass. The dosing rate of 1 wt % Fe was not carried forward to field trials, due to a high estimated cost for full-scale implementation at this dosing level.

Field Plot Study

Soils in the field plots, analyzed before Fe treatments, contained an average of 790 mg kg^{-1} of As_{TOT} , and 30 mg kg^{-1} of As_{BAC} (4% of As_{TOT}) (Table 3.3). Total Fe in soils averaged 89.7 mg g^{-1} (9 wt %), whereas Fe dissolved in the SBRC-g extract (Fe_{BAC}) averaged 1450 mg kg^{-1} (1.6% of Fe_{TOT}). Consistent with bench-scale treatability testing, field-scale testing of Fe + lime amendments produced significant reductions in As_{BAC} . At the first post-treatment sampling point, 60 d post treatment, FeCl_3 -amended soils at 0.25 and 0.5 wt % Fe-equivalent dosing rates showed 44% and 75% reductions in As_{BAC} as compared to controls (Table 3.3, Figure 3.1). FeSO_4 -amended soils showed less reduction in As_{BAC} (9% and 18% reductions versus control, at the two dosing rates) than FeCl_3 amended soils. At 336 d post treatment, performance of FeCl_3 and FeSO_4

substrates in reducing A_{SBAC} were nearly identical, with 33-36% reduction in A_{SBAC} for 0.25 wt % Fe dosing and 60-62% reduction in A_{SBAC} for 0.5 wt % Fe dosing. Performance at 612 d post treatment was comparable with that after 336 d, with 30-41% reduction in A_{SBAC} for 0.25 wt % Fe dosing and 59-63% reduction for 0.5% Fe dosing. Triplicate multi-increment samples were collected from each field plot during this final sampling event (612 d post treatment), to allow statistical comparison of results. Replicate (triplicate) sample results and summary statistics for this final sampling event are provided in Table 3.4. The A_{SBAC} of control soil averaged 27.1 mg kg⁻¹. Soils amended with 0.25 wt % Fe (FeCl₃ and FeSO₄) exhibited similar A_{SBAC} at 18.9 and 16.0 mg kg⁻¹. Soils amended with 0.5 wt % Fe showed lower A_{SBAC} for FeCl₃ and FeSO₄ of 11.1 and 10.1 mg kg⁻¹. Student's *t*-tests were conducted to determine statistical significance of results (Table 3.5). The means of sample results for Fe-treated soils were all statistically different than the control soil at a 95% confidence level. Only the 0.5 wt % FeCl₃ and 0.5 wt % FeSO₄ results were similar enough to one another that they could not be statistically differentiated at the 95% confidence level.

Fe_{TOT} and Fe_{BAC} in post-treatment soils were higher than in un-amended control soils, as expected based on Fe amendments. The Fe_{TOT} concentration, as measured in the <0.25 mm soil fraction used for *in vitro* bioaccessibility testing, was significantly higher than the concentration of Fe added to bulk soil in the field test plot (<5 mm grain size). The average Fe_{TOT} in control soils was measured at 9.0 wt %. In soil with 0.25 wt % Fe added to bulk soil, the average Fe_{TOT} in the <0.25 mm fraction was 10.4%; an increase of 1.4 wt % Fe. For soils with 0.5 wt % Fe added, the average Fe_{TOT} in <0.25 mm fraction was 12.2 wt %, and increase of 3.2 wt % Fe compared to control. This represents an accumulation of Fe_{TOT} in the <0.25 mm soil fraction some 5 to 6 times greater than the bulk soil amendment dosing rate, indicating Fe accumulation in the finer soil fraction. Bioaccessible Fe, the Fe extracted from soil during the SBRC-g test, averaged 1447 mg kg⁻¹ (or 1.6% of Fe_{TOT}) in pre-amendment soils (Table 3.3). In post-treatment soils, Fe_{BAC} was elevated as compared to un-amended control soils (Table 3.3, Figure 3.2). At 60 d post treatment, from 4.9 to 8.8 wt % of Fe_{TOT} was extracted in the SBRC-g test; and soils amended with FeSO₄ showed much higher Fe_{BAC} levels than those amended with FeCl₃. By 612 d post treatment, A_{SBAC} levels were below 3% of Fe_{TOT} for all treated soils, but Fe_{BAC} was still slightly higher in FeSO₄ amended soils than FeCl₃ amended soils.

Replicate field samples were collected from the control plot during the course of the field pilot test. During the four sampling events (0, 60, 336 and 612 d) a total of 8 multi-increment samples were collected from the test plots for analysis. Coefficient of variance (CV, standard deviation divided by mean) for these replicate samples (N=8) was calculated for the key analytical parameters as follows: A_{STOT} (CV 3.7%), Fe_{TOT} (CV 5.3%), A_{SBAC} (CV 6.8%) and Fe_{BAC} (CV 16.8%). The variance in analysis of field

sampling replicates includes errors introduced by field sampling procedures (multi-increment sampling), laboratory subsampling (riffler splitting or multi-increment), laboratory digestions or *in vitro* extractions, and analytical procedures (ICP, ICPMS).

X-ray Absorption Spectroscopy Results

Samples of the 0.5% FeCl₃ amended soil and control soil were collected 135 d post treatment and evaluated by XAS to determine As speciation and As solid phase associations. X-ray adsorption near edge structure (XANES) spectra (Figure 3.3) indicate that As is present in both soils as arsenate (As(V)) based on absorption maxima at 11,874 eV. Radial structure functions are shown in Figure 4 with the raw data represented as solid black lines and experimental fitted data as red dots. X-ray adsorption fine structure (XAFS) analysis indicates no difference in the As speciation between FeCl₃ treated and control soils. Structural parameters for the first shell (As-O) indicate a coordination number (CN) of 4 with a interatomic bond distance (R) of approximately 1.68 Å. The second shell for As-Fe scattering suggests a CN of 2 and R of 3.28-3.31 Å. These parameters (Table 3.6) point to arsenate speciation as bidentate binuclear complexes, consistent with arsenate ligand exchange sorption to Fe oxyhydroxides (Wang and Mulligan, 2008).

Targeted Extractions, pH and Redox Measurements

Fe treated and control soils collected nearly 1 y after treatment (336 d) were evaluated for key soil properties including CD-extractable Fe, pH and oxidation-reduction potential (redox), along with SBRC-g testing previously described. The pH of treated soils ranged from 6.3 to 7.0, higher than the pH of 5.5 observed for control soils (Table 3.7). Oxidation-reduction (redox) potential of treated soils ranged from Eh of 482 mV to 528 mV, slightly lower than the control soil Eh of 543 mV. Citrate-dithionite-extractable Fe ranged from 57 to 74 mg g⁻¹ in treated soils, higher than in controls soils (43 mg g⁻¹).

Phosphate Amendments

Dissolved PO₄ added to <2 mm fractions of Fe treated and untreated soils (samples from 336 d post treatment) in laboratory treatability tests caused a substantial increase in AS_{BAC} (measured in <0.25 mm fraction) measured two weeks after P addition (Table 3.8). For control soils (no Fe amendments), increase in AS_{BAC} was linearly proportional to the PO₄ dosing rate (Figure 3.5). AS_{BAC} measured at 28 mg kg⁻¹ with no PO₄ addition increased to 69 mg kg⁻¹ at the maximum dosing rate of 1500 mg P kg⁻¹ soil, an increase of nearly 150%. For Fe-treated soils, the AS_{BAC} levels prior to PO₄ addition were 12 to 13 mg kg⁻¹, a increased linearly with respect to PO₄ dosing levels. However, at the maximum PO₄ dose of 1500 mg P kg⁻¹ soil, AS_{BAC} increased to 28 mg kg⁻¹ in FeCl₃ amended soils and 31 mg kg⁻¹ in FeSO₄ amended soils, representing 114% and 153% increases in AS_{BAC} over soils with no PO₄ addition. These percentage increases in AS_{BAC} are comparable to the increase observed in control soil. In summary, PO₄ addition increased AS_{BAC} in both control and Fe-amended soils.

Bioaccessible P (P extracted in the SBRC-g test) increased in proportion to P dosing (Table 3.8, Figure 3.6), similar to the observed increase in As_{BAC} but at an even greater rate on a percentage basis. At the maximum PO_4 dose of $1500 \text{ mg P kg}^{-1}$ soil, P_{BAC} increased nearly 700% in control (no Fe amendments) and $FeSO_4$ -amended soils as compared to soils without PO_4 addition. In $FeCl_3$ -amended soils, P_{BAC} in the highest PO_4 -dosed soil increased less, but still more than 400% more than soils without PO_4 addition.

3.4 Discussion

Formation of Fe Substrate

Several lines of evidence indicate that Fe-amendments in study soils result in the formation of supplemental Fe oxyhydroxide substrate with As sorption capacity that also reduces As bioaccessibility. Control soils and iron-treated soils were qualitatively inspected by transmission electron microscopy. Treated soils appeared to contain a larger proportion of finely-crystalline to non-crystalline iron phases with ferrihydrite-like morphology. The new Fe compounds formed in soil amended with both $FeCl_3$ and $FeSO_4$ are selectively dissolved by the citrate-dithionite targeted extraction technique, indicating they are likely oxyhydroxides similar to naturally-occurring pedogenic phases (ferrihydrite, goethite). Both Fe_{TOT} and Fe_{CD} were analyzed in soils collected 336 d post treatment. Fe_{TOT} in soil treated with 0.25 and 0.5 wt % Fe was measured to have increased by an average of 14.7 and $30.7 \text{ mg Fe g}^{-1}$ soil compared to control (average of both $FeCl_3$ and $FeSO_4$ amended soils at each Fe-dosing rate, Table 3.3). Reactive (CD-extractable) Fe in these same soils, treated with 0.25 and 0.5 wt % Fe, was measured to have increased by an average of 15.1 and $32.5 \text{ mg Fe g}^{-1}$ soil compared to control (Table 3.5). These results indicate that virtually all of the Fe introduced into soils by $FeCl_3$ and $FeSO_4$ amendments was in the “reactive” state, likely composed of oxyhydroxide solid phases that strongly sorb phosphate and arsenite/arsenate.

Iron substrates became progressively more recalcitrant over time, as measured by Fe dissolved by the *in vitro* extract (Fe_{BAC}). Sixty days after treatment, a large fraction of the Fe added to soils remains soluble in the *in vitro* acid extract, especially for the $FeSO_4$ treated soil (Figure 3.2). By 336 d post treatment, Fe_{BAC} in $FeCl_3$ and $FeSO_4$ -amended soils are nearly identical, and at the final sampling event (612 d) the Fe_{BAC} levels are not statistically different at the 95 percent confidence level (Student's *t*-Test, $p < 0.05$). These data indicate that ferric oxyhydroxide solid phase materials are becoming more recalcitrant over time, and less likely to be dissolved in the SBRC-g *in vitro* extract (1.5 pH). This may be due to a progressive increase in crystallization and reduction in surface area of the ferric solid phase materials.

The high solubility of Fe in $FeSO_4$ -amended soils 60 d post treatment is not completely understood. It may be that $FeSO_4 \cdot 7H_2O$ granular solids added to the soil have not

completely dissolved, however there was no physical evidence of residual ferrous sulfate salts, and screening by X-ray diffraction did not indicate the presence of a ferrous sulfate heptahydrate solid phase. It is possible that Fe dissolved from ferrous sulfate forms an incipient solid phase that is more soluble than the solid phase formed by Fe dissolved from FeCl_3 , after that 2 month incubation period. By one year post treatment, the Fe substrates for both FeCl_3 and FeSO_4 -amended soils appear to be similarly recalcitrant.

Arsenic binding to Fe Substrate

The reduction in A_{SBAC} observed in Fe-amended soils is believed to be the result of increased sorption of As on newly-formed Fe oxyhydroxide solids. XAFS analysis indicates arsenate bonding to an Fe oxyhydroxide substrate, in both control and Fe-treated soils, with no evidence of Fe arsenate mineral formation. In our previous work with historically-contaminated soils (Chapter 2), within a single soil type we observed a higher percentage of A_{SBAC} at higher As contaminant concentrations, suggesting limits to the sorption capacity of the soil substrate (see Chapter 2). Conversely, for soils with similar As contaminant concentrations, those with higher concentrations of reactive Fe (Fe_{CD}) substrate have lower A_{SBAC} . These observations suggest that A_{SBAC} can be lowered by increasing the Fe substrate content of the soil. By way of Fe amendments, additional Fe oxyhydroxide substrate is formed, and A_{SBAC} is effectively reduced.

As described above, 60 d after treatment, the FeSO_4 -amended soil had formed less recalcitrant Fe substrate than the FeCl_3 -amended soil, and reductions in A_{SBAC} in FeSO_4 -amended soils were less than those of FeCl_3 -amended soils. By 336 d post treatment, Fe_{BAC} and A_{SBAC} in FeCl_3 and FeSO_4 -amended soils are at similar levels, and the two treatment reagents appear can be considered similarly effective. At 612 d post treatment, Fe_{BAC} and A_{SBAC} are lower yet, however our study was not extended beyond that time period and it is unclear whether further reductions in A_{SBAC} would occur. Several processes may be occurring over time to lower A_{SBAC} in Fe-treated soils. These include redistribution of arsenate from the pre-existing substrate to the newly-formed Fe oxyhydroxide solids, progressive crystallization of Fe oxyhydroxides to more recalcitrant forms, and an increase in occluded arsenate within substrates. Previous studies (Yang et al., 2002; Quazi et al., 2010) have shown that As added to soil substrates will become progressively less bioaccessible over time. We are not aware of any studies showing the long-term (multi-year) effects of Fe amendments on A_{SBAC} , however our field trials that were evaluated for nearly a two year period indicate that this technology may be a viable long-term remedy for As-contaminated soils.

Potential Full-scale Implementation

Full-scale implementation of Fe amendment soil treatment is feasible using conventional construction and farming equipment, utilizing deep tillage to provide adequate mixing of chemical reagents. Based on efficacy of this treatment in the field plots, the remedy is expected to reduce A_{SBAC} by 25 to 50 percent. Ferrous sulfate heptahydrate is the

recommended Fe source, because of lower cost and ease of application as compared to ferric chloride. Based on the current costs in Hawaii for labor, equipment and chemicals (ferrous sulfate heptahydrate and lime), full-scale soil treatment at 0.5 wt % Fe dosing to a depth of 60 cm is estimated to cost approximately \$60,000 (US) per hectare or \$10 per m³ of treated soil. This compares favorably to the current landfill disposal cost on the Island of Hawaii of approximately \$100 (US) per m³. In addition to lower cost, an in-situ iron treatment remedy provides additional benefit by not consuming limited landfill space that is currently needed for municipal solid waste disposal purposes.

Fe amendments to reduce As_{BAC} may be particularly useful in soils with low levels of naturally-occurring Fe substrates. Soils with low pedogenic Fe content in Hawaii include very young soils (Udifolists), certain subsoils with high lithic content, and carbonate-rich soils in coastal areas. Subsoils with low Fe_{CD} and high lithic content, from a site in Hilo, (Table 2.3, sample IDs 62-64) show $As_{BAC\%}$ ranging from 37 to 52%, at the high end of the measured range for volcanic-derived soils. Bioaccessible arsenic greater than 50% of As_{TOT} has been reported by HDOH staff for carbonate-rich “cap rock” soils on the Island of Oahu (R. Brewer, pers. comm.). Most soils outside of Hawaii have lower pedogenic Fe content than Hawaiian volcanic-derived soils, and Fe amendments to increase adsorptive Fe solid phases and reduce As_{BAC} may be beneficial. For example, much lower Fe_{CD} content is observed in suites of U.S. and Australian soils from studies of Yang et al. (2002) and Juhasz et al. (2007) than in Hawaii soil of this study (Figure 2.8).

Conditions Potentially Increasing Bioaccessible Arsenic

The two geochemical processes that could most likely lead to increased As_{BAC} in iron-treated and untreated soils are dissolution of the ferric iron substrate due to low pH or reductive solubilization under low O₂ conditions, and competitive displacement of arsenate by PO₄. Ferric oxyhydroxide solid phases are stable at the observed pH and likely redox conditions observed for treated and untreated soils. Natural or human-induced conditions are unlikely to drive these soils into the pH/redox field where ferric oxides become unstable (Figure 7). Reducing environments, such as can develop under flooded conditions, can result in reductive dissolution of ferric oxyhydroxides and the concurrent release of As or other sorbed species (Berg et al., 2001; Swartz et al, 2004). However, ferric oxyhydroxide dissolution is unlikely for the Hydrudand soils of the study area. First, the soils are highly permeable and typically well drained, due to porous lava rock beneath approximately 1 m of soil accumulation. In addition, the high concentration of reactive Al (oxalate-extractable Al) in these volcanic ash-derived soils (USDA-NRCS, 2011) may have an inhibitory effect on iron reduction, even in submerged conditions (Shoji et al., 1993).

Although ferric iron reduction and associated release of sorbed As is unlikely to occur in study soils, the application of phosphate fertilizers to iron treated soils (or untreated soils) by gardening, commercial agriculture or landscaping practices is a plausible

circumstance. Applied PO_4 could result in increased As_{BAC} , as shown in laboratory treatability tests of this study. It should be noted that our treatability test used dissolved PO_4 , resulting in high pore water (soil solution) concentrations of PO_4 . Typical agricultural fertilizers, such as rock phosphate, treble superphosphate, or ammonium phosphate, are likely to result in a more sustained release of PO_4 to the soil solution. The effect of different fertilizer compounds, at a range of application rates, on As_{BAC} cannot be inferred from our preliminary bench-scale treatability testing. Further work on this area of potential environmental hazard is warranted, especially in areas where former sugar cane lands are being used for private or commercial agriculture. We emphasize that phosphate addition to As-contaminated soils has the potential to significantly increase As_{BAC} , whether or not the soils have been Fe treated. In selecting a robust remedy for reduction of As_{BAC} using Fe amendments, institutional controls to prevent phosphate fertilizer application should be considered as a component of the remedy.

3.5 Conclusions

Former sugar cane lands on the Island of Hawaii contain elevated levels of total and bioaccessible As. Human health risk from incidental ingestion of As-contaminated soil could be reduced at certain sites by soil amendments. Previous studies have shown that Fe amendments can reduce the leachability, bioavailability (plant uptake), and *in vitro* bioaccessibility of As in soil. Results of long-term (more than 1 year) field-scale studies of Fe amendments to reduce As_{BAC} have not previously been published. Our study demonstrates that reagent mixture of either ferrous sulfate plus lime or ferric chloride plus lime will effectively reduce As_{BAC} in volcanic-derived Andisols of Hawaii. At a dosing rate of 0.5 wt % Fe per dry weight soil, As_{BAC} was reduced in field plots by approximately 60% after nearly one year post treatment. Ferrous sulfate plus lime did not perform as well as FeCl_3 plus lime as measured 60 d post treatment, but performed similarly as of the 336 d sampling event. The delayed efficacy of FeSO_4 versus FeCl_3 is not fully understood. Fe amendments are believed to result in the formation of additional reactive Fe substrate in the soil, strongly sorbing As and preventing its release in the *in vitro* bioaccessibility test. Transmission electron microscopy and targeted chemical dissolution (citrate-dithionite) indicate that the introduced Fe is present as a reactive Fe oxyhydroxide substrate. X-ray adsorption spectroscopy indicates that all As is in the oxidized state (As(V)), and bonding of As in both Fe-treated and control soils is consistent with ligand exchange sorption to Fe oxyhydroxides. Addition of dissolved phosphate to both Fe-treated and control soils increases As_{BAC} . Use of phosphate fertilizers on As-contaminated lands may increase the human health risk from incidental ingestion of soil. Fe-amendment remedies to reduce As_{BAC} in soil may be more cost effective than a traditional excavation and landfill disposal remedy, and should be considered if the remedial goals are reduction of direct exposure risk.

3.6 References

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Table 3.1 Test Plot Soil Properties, <0.25mm fraction, air-dried basis

Soil Type	pH^a	TOC^b wt %	LOI %	As_{TOT}^c (mg kg⁻¹)	As_{BAC}^d (mg kg⁻¹)	Fe_{TOT}^e (mg g⁻¹)	Fe_{CD}^f (mg g⁻¹)
Hydrudands	5.6 ± 0.1	11.1 ± 0.1	33	790 ± 50	30 ± 3	89.7 ± 1.2	43 ± 0.5

Uncertainties expressed are ± 1 stdev based on replicate analyses

^a pH by 1:1 soil water slurry

^b Total organic carbon, coefficient of variance of replicate analyses

^c Total As by acid digestion and ICPMS analysis

^d SBRC-gastric method, <0.25 mm fraction air-dried soil

^e Total Fe by acid digestion and ICPOES analysis

^f Fe in citrate-dithionite extract, measured by ICPOES

Table 3.2 Bench-scale Fe Amendment Treatability Study Results

Amendment	Dose ^{b,c} wt. %	In Vitro Analysis ^a			As _{BAC}
		As _{TOT} ^d (mg kg ⁻¹)	As _{BAC} ^e (mg kg ⁻¹)	As _{BAC} ^f (%)	% Reduction vs. Control ^e
Control	none	580	92	16%	-
FeCl ₃ + lime	0.25%	570	75	13%	18%
FeCl ₃ + lime	0.5%	590	64	11%	31%
FeCl ₃ + lime	1%	580	45	8%	51%
FeSO ₄ + lime	0.25%	680	91	13%	1%
FeSO ₄ + lime	0.5%	670	87	13%	6%
FeSO ₄ + lime	1%	640	72	11%	22%

^a SBRC-g method, <0.25 mm fraction air-dried soil

^b Fe addition to <2 mm fraction air-dried soil, weight percent basis

^c Ca(OH)₂ added at dosing rate of 1.5 moles/mole Fe added

^d Total digestion by EPA 3050B, relative error 6% (coefficient of variation, CV)

^e As_{BAC} (concentration basis), relative error approximately 9% (CV)

^e Bioaccessible As as percentage of As_{TOT}. Relative error approx. 11% (CV)

^e Percent reduction in As_{BAC} (concentration basis) compared to control soil

Table 3.3 Field Plot - Fe Amendment Treatability Study Results

Sampling Event Dose ^{3,4}	Total Digestion ^a			In Vitro Analysis ^e				
	As _{TOT} ^b (mg kg ⁻¹)	Fe _{TOT} ^c (mg g ⁻¹)	ΔFe _{TOT} ^d (mg g ⁻¹)	As _{BAC} ^f (mg kg ⁻¹)	As _{BAC%} ^g (% of As _{TOT})	ΔAs _{BAC} ^h (% Reduction)	Fe _{BAC} ⁱ (mg kg ⁻¹)	Fe _{BAC%} ^j (% of Fe _{TOT})
Pre-Treatment								
0.25% FeCl ₃	778	89.0	-	31	4.0%	-	1500	1.7%
0.50% FeCl ₃	772	89.7	-	31	4.0%	-	1490	1.7%
0.25% FeSO ₄	776	90.9	-	30	3.9%	-	1420	1.6%
0.50% FeSO ₄	783	89.0	-	28	3.5%	-	1400	1.6%
Control	839	90.0	-	28	3.4%	-	1420	1.6%
Mean ± 1 stdev	790 ± 30	89.7 ± 0.8		30 ± 1.7	3.8 ± 0.3%		1450 ± 50	1.6 ± 0.1%
60 Days Post Treatment								
0.25% FeCl ₃	705	103	12.4	17	2.5%	44%	5040	4.9%
0.50% FeCl ₃	730	128	36.9	8	1.1%	75%	6340	5.0%
0.25% FeSO ₄	710	109	18.2	28	3.9%	9%	5650	5.2%
0.50% FeSO ₄	648	122	31.4	25	3.9%	18%	10800	8.8%
Control	872	90.8	-	31	3.5%	-	1620	1.8%
336 Days Post Treatment								
0.25% FeCl ₃	792	101	12.6	20	2.6%	33%	3400	3.4%
0.50% FeCl ₃	793	121	32.6	12	1.5%	60%	4780	3.9%
0.25% FeSO ₄	805	106	16.9	19	2.4%	36%	2980	2.8%
0.50% FeSO ₄	756	117	28.7	11	1.5%	62%	3790	3.2%
Control	854	88.6	-	30	3.5%	-	1460	1.6%
612 Days Post Treatment⁶								
0.25% FeCl ₃	775	99.9	9.2	19	2.4%	30%	2840	2.8%
0.50% FeCl ₃	761	119	28.7	11	1.5%	59%	3460	2.9%
0.25% FeSO ₄	794	104	13.6	16	2.0%	41%	2130	2.0%
0.50% FeSO ₄	812	121	30.4	10	1.2%	63%	2930	2.4%
Control	843	90.7	-	27	3.2%	-	1090	1.2%

^a Total digestion by EPA 3052-equivalent, on air-dried <0.25 mm soil fraction

^b Replicate measurements of As_{TOT} indicate relative error (coefficient of variance, CV) of 3%, see Table 3.4

^c Replicate measurements of Fe_{TOT} indicate relative error (CV) of 1.3%

^d ΔFe_{TOT} is difference between treated plot and control plot for subject sampling event

^e SBRC-g in vitro method, on air-dried <0.25 mm soil fraction

^f Replicate measurements of As_{BAC} indicate relative error (CV) of 5%

^g Relative error (CV) of As_{BAC%} is 6%, considering propagation of errors in As_{TOT} and As_{BAC}

^h ΔAs_{BAC} is difference between treated plot and control plot for subject sampling event

ⁱ Replicate measurements of Fe_{BAC} indicate relative error (CV) of 2%

^j Relative error (CV) of Fe_{BAC%} is 2%, considering propagation of errors in Fe_{TOT} and Fe_{BAC}

Table 3.4 Replicate Sampling Data and Error Statistics, Final Sampling Event (612 d)

Amendment	As _{TOT} ^a						Fe _{TOT} ^a					
	Rep1	Rep2	Rep3	Ave	StDev	CV ^c	Rep1	Rep2	Rep3	Ave	StDev	CV
0.25% FeCl ₃	801	752	772	775	25	3%	100	98.4	101	99.9	1.5	1.5%
0.50% FeCl ₃	754	758	771	761	9	1.2%	120	120	118	119	1.1	0.9%
0.25% FeSO ₄	771	811	801	794	21	3%	103	106	104	104	1.4	1.3%
0.50% FeSO ₄	834	784	819	813	25	3%	122	119	122	121	1.8	1.5%
Control	859	817	853	843	23	3%	91.4	89.3	91.3	90.7	1.2	1.3%
					Ave CV	3%					Ave CV	1.3%

Amendment	As _{BAC} ^b						Fe _{BAC} ^b					
	Rep1	Rep2	Rep3	Ave	StDev	CV	Rep1	Rep2	Rep3	Ave	StDev	CV
0.25% FeCl ₃	20	19	18	19	1.3	7%	2850	2810	2870	2840	30	1.1%
0.50% FeCl ₃	11	12	11	11	0.5	5%	3510	3530	3350	3460	100	2.9%
0.25% FeSO ₄	15	16	17	16	0.6	4%	2070	2210	2120	2130	70	3.3%
0.50% FeSO ₄	11	10	10	10	0.4	4%	2810	3000	2920	2910	100	3.4%
Control	27	26	29	27	1.5	6%	1110	1080	1090	1090	15	1.4%
					Ave CV	5%					Ave CV	2%

Triplicate multi-increment sampling of field plots (Rep1, Rep2, Rep3) at final sampling event (612 d post treatment)

^a EPA method 3052 digestion, <0.25 mm fraction air-dried soil

^b SBRC-g method, <0.25 mm fraction air-dried soil, analysis of As and Fe by ICPMS

^c Coefficient of variation (CV), stdev divided by mean (also referred to as "relative standard deviation")

Table 3.5 Field Plot - Replicate Sampling Data, Student's *t*-Test, Final Samping Event

Student's *t*-Test, unpaired, two-tailed

Null hypothesis: Both populations have same mean

P values: <0.05 indicates null hypothesis is rejected at 95% confidence level

	0.25% FeCl ₃	0.50% FeCl ₃	0.25% FeSO ₄	0.50% FeSO ₄	Control
0.25% FeCl ₃	-	-	-	-	-
0.50% FeCl ₃	0.001	-	-	-	-
0.25% FeSO ₄	0.025	0.000	-	-	-
0.50% FeSO ₄	0.000	0.051	0.000	-	-
Control	0.002	0.000	0.000	0.000	-

Table 3.6 Structural Parameters from XAFS Analysis

Sample	Shell	CN	R	δ^2
Control	As-O	4.00	1.70	0.002
	As-Fe	1.95	3.31	0.005
0.50% FeCl ₃	As-O	4.00	1.68	0.002
	As-Fe	2.10	3.28	0.003

Data and analysis by K. Scheckel, USEPA

Table 3.7 Soil Properties, 336 Days Post Treatment

Dose ^a	pH ^b	Eh ^c (mV)	Fe _{CD} in soil ^d (mg g ⁻¹)	ΔFe _{CD} ^e (mg g ⁻¹)	ΔFe _{CD} ^e (%)	Fe _{BAC} in soil ^f (mg g ⁻¹)
Control	5.5	543	43	-	-	1.5
0.25% FeCl ₃	6.3	511	57	14	34%	3.4
0.50% FeCl ₃	6.0	528	77	34	80%	4.8
0.25% FeSO ₄	6.4	508	58	16	37%	3.0
0.50% FeSO ₄	7.0	482	74	31	73%	3.8

^a Fe addition to bulk soil, air dry weight percent, Ca(OH)₂ added at 1.5 moles/mole Fe

^b pH in 1:1 soil:DI water slurry, coefficient of variation (CV) of replicate analyses is 0.9%

^c Oxidation-reduction potential measured in field-moist soils, CV of replicate analyses is 1.5%

^d Citrate-dithionite extract analyzed for Fe by ICPOES, CV of replicate analyses is 1.2%.

^e Change in Fe_{CD} content compared to control

^f SBRC-g extract analyzed for Fe by ICPMS, CV of replicate analyses is 2%

Table 3.8 Phosphate Amendment Study Results

Dose P ^a mg kg ⁻¹	As _{TOT} ^b mg kg ⁻¹	As _{BAC} ^c mg kg ⁻¹	As _{BAC} %	% Increase in As _{BAC} ^d	P _{TOT} ^e mg kg ⁻¹	P _{BAC} ^f mg kg ⁻¹	P _{BAC} %	% Increase ^d in P _{BAC}
0	666	12	1.8%	-	2200	55	2.6%	-
240	699	16	2.3%	31%	2600	97	3.7%	75%
600	695	19	2.7%	54%	3100	170	5.7%	206%
1500	715	31	4.3%	153%	4100	430	10%	675%

^a P added to <2mm soil fraction, air dry weight equivalent, soils were collected 336 d post treatment

P spikes were KH₂PO₄ dissolved in DI water, added to field-moist soils

As_{TOT}, As_{BAC}, P_{TOT}, P_{BAC} measured in <0.25 mm soil fraction

^b Duplicate measurements of As_{TOT} showed relative percent difference (RPD) of 7.0%

^c Duplicate measurements of As_{BAC} showed relative percent difference (RPD) of 2.7%

^d Compares P-treated soil with control soil (no P amendment)

^e Duplicate measurements of P_{TOT} showed relative percent difference (RPD) of 5.0%

^f Duplicate measurements of P_{BAC} showed relative percent difference (RPD) of 1.1%

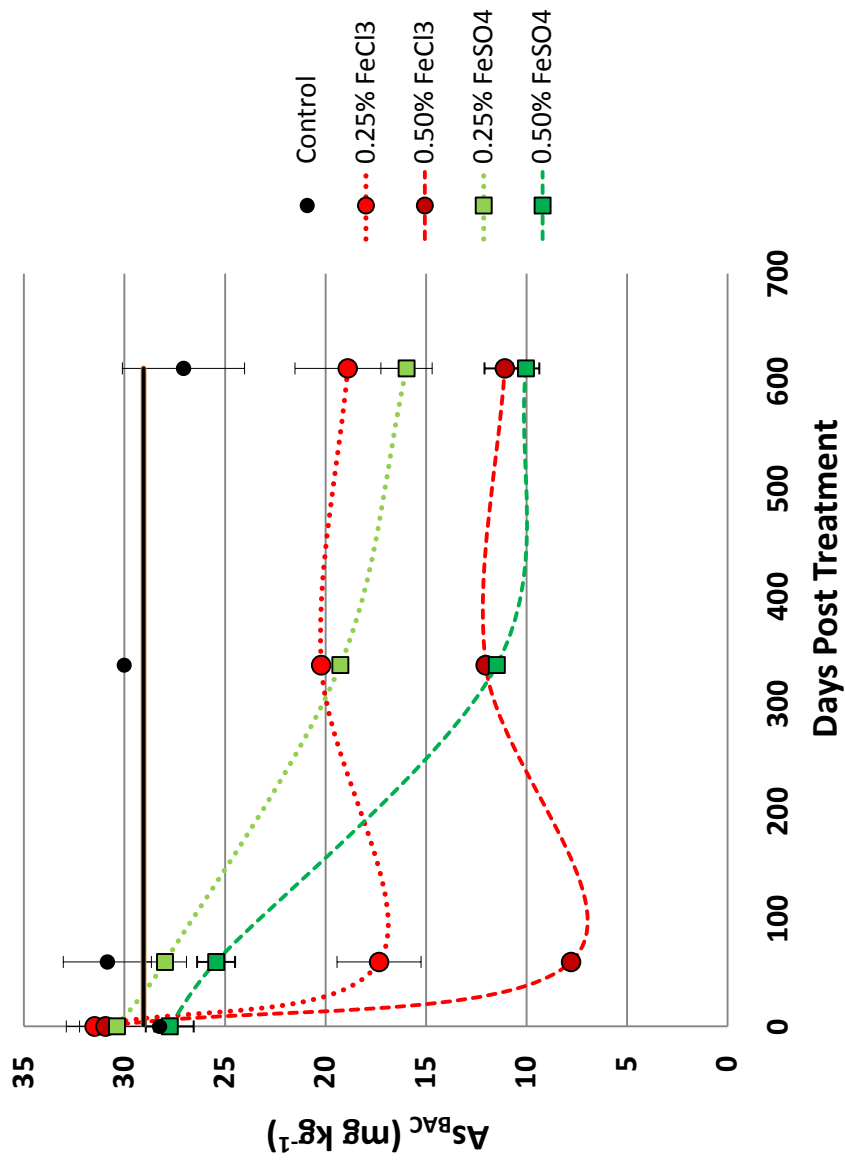


Figure 3.1 Bioaccessible As in amended and control soils. Error bars for 0 day (pre-treatment) and 60 day samples show range of duplicate field multi-increment (MI) samples. Error bars for final (612 day) samples are 2 stdev of triplicate MI samples. As_{BAC} of control shown as constant.

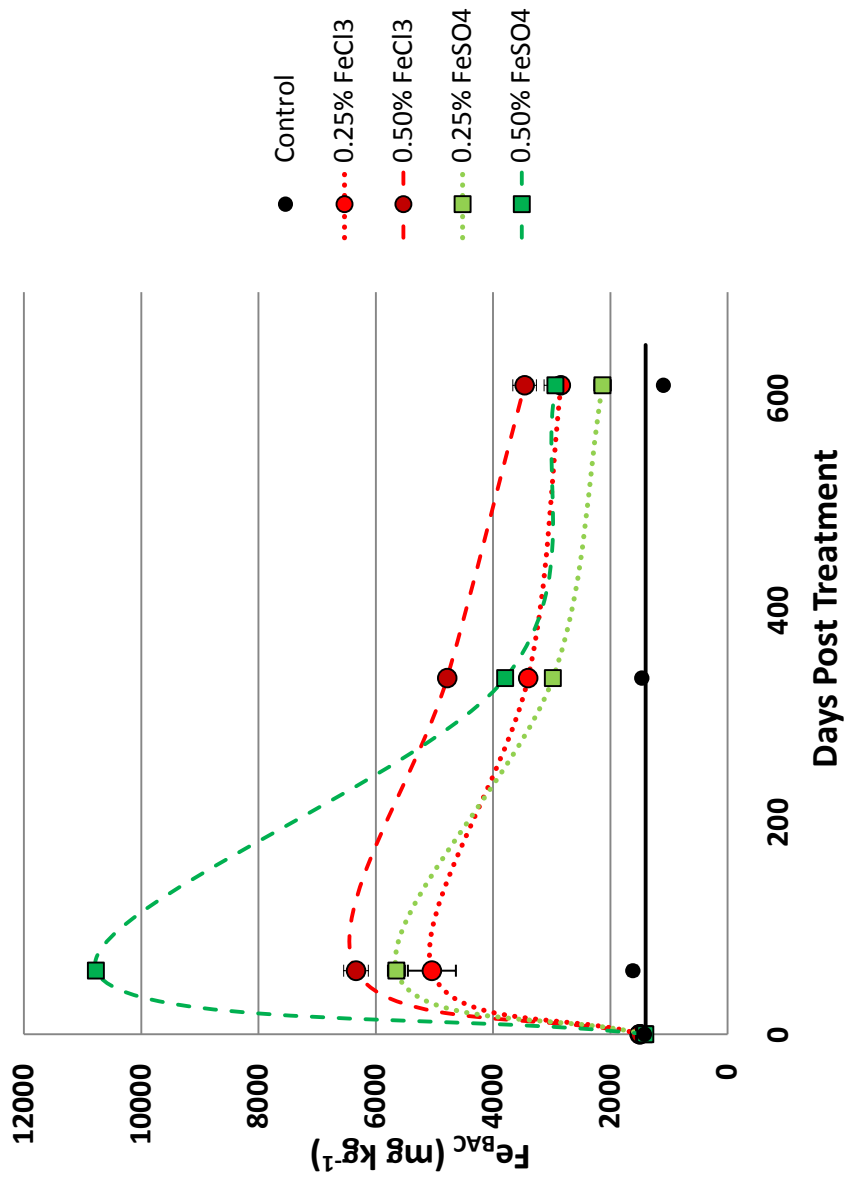


Figure 3.2 Bioaccessible Fe in amended and control soils. Error bars for 0 day (pre-treatment) and 60 day samples show range of duplicate field multi-increment (MI) samples. Error bars for final (612 day) samples are 2 stdev of triplicate MI samples. As_{BAC} of control shown as constant.

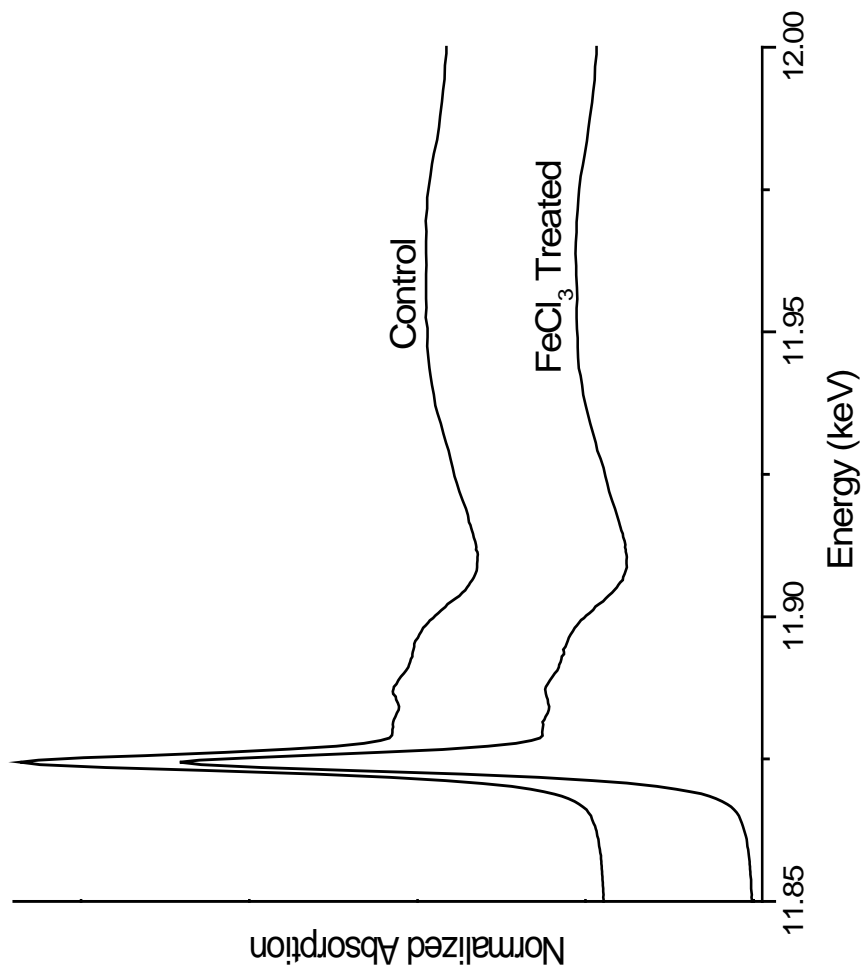


Figure 3.3 XANES spectra for FeCl₃-treated and control soils. No difference in As speciation is evident from comparison of spectra. Data and analysis by K. Scheckel, USEPA

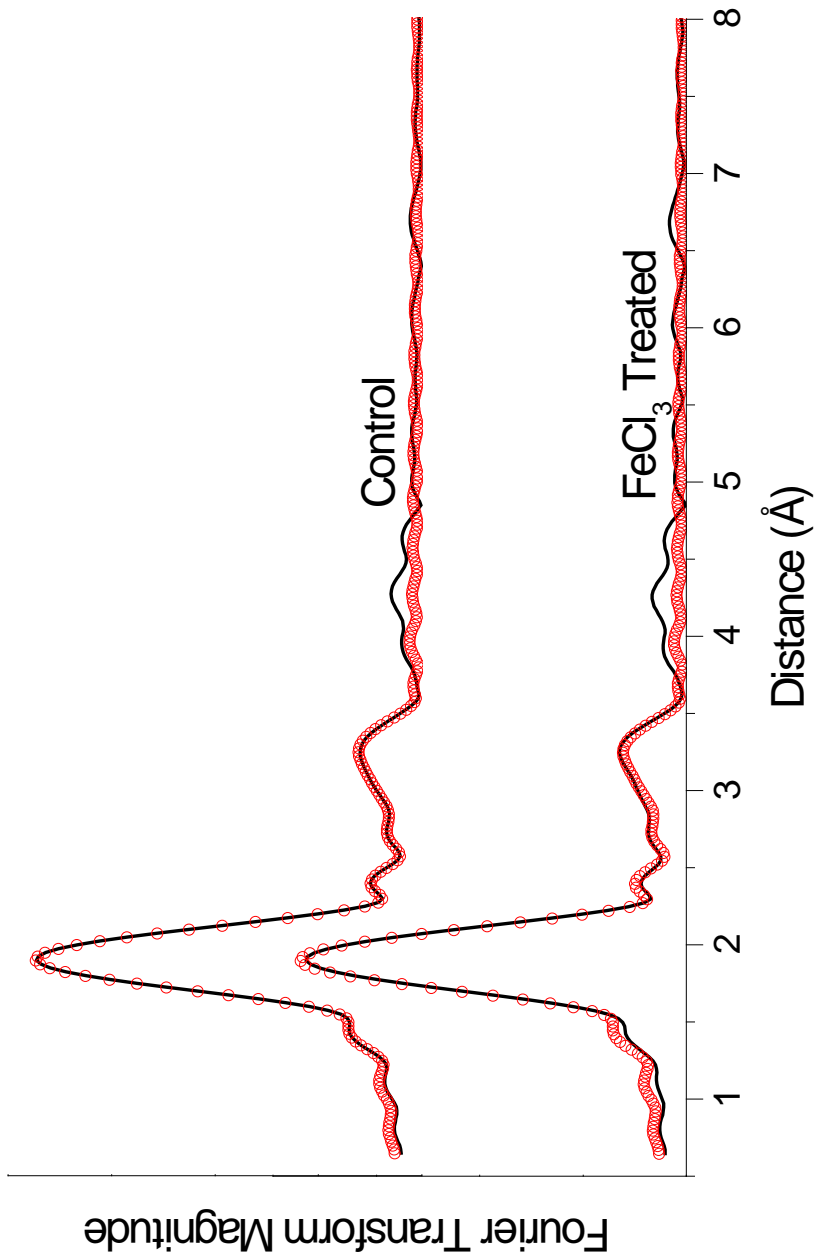
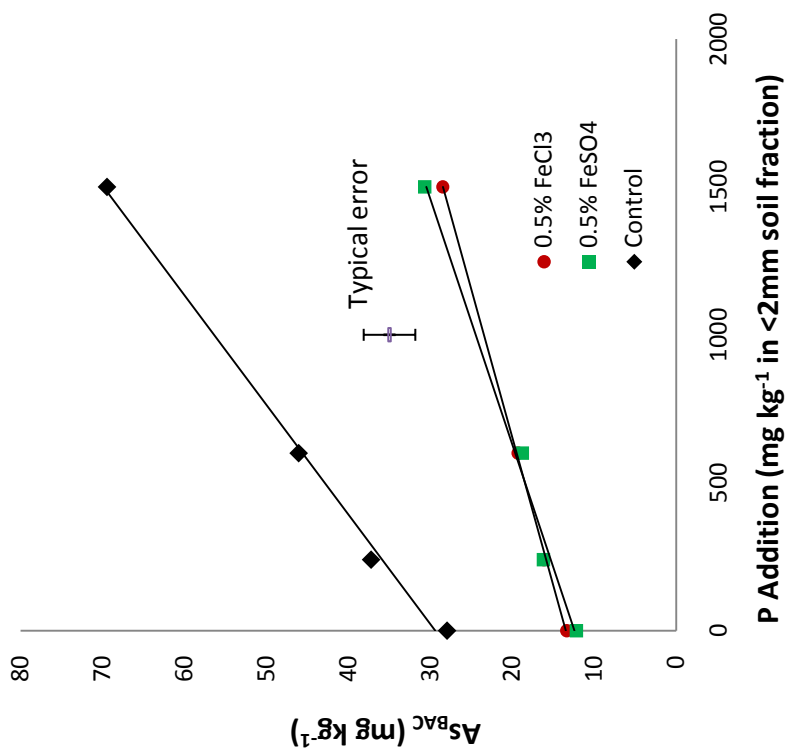
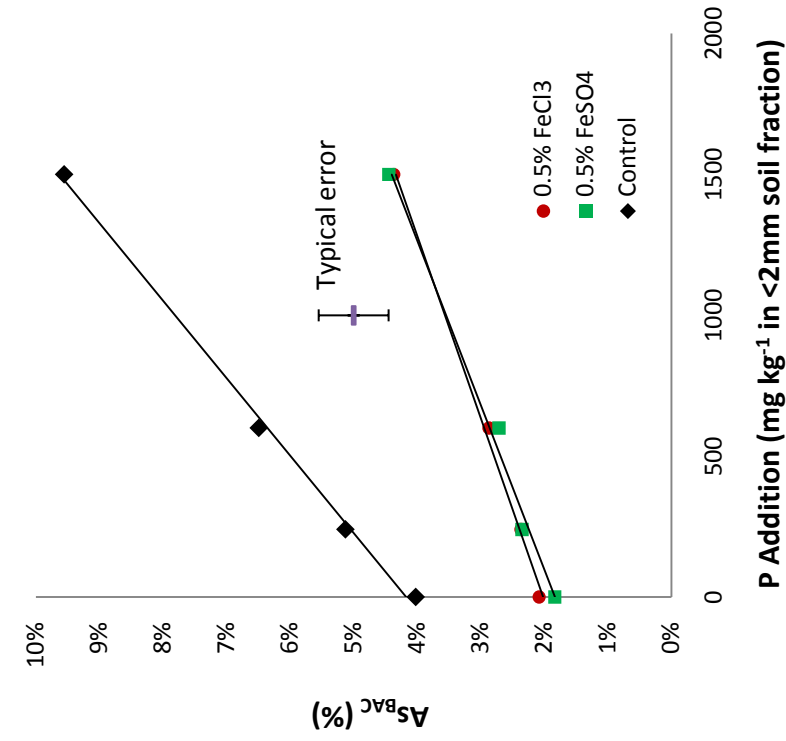
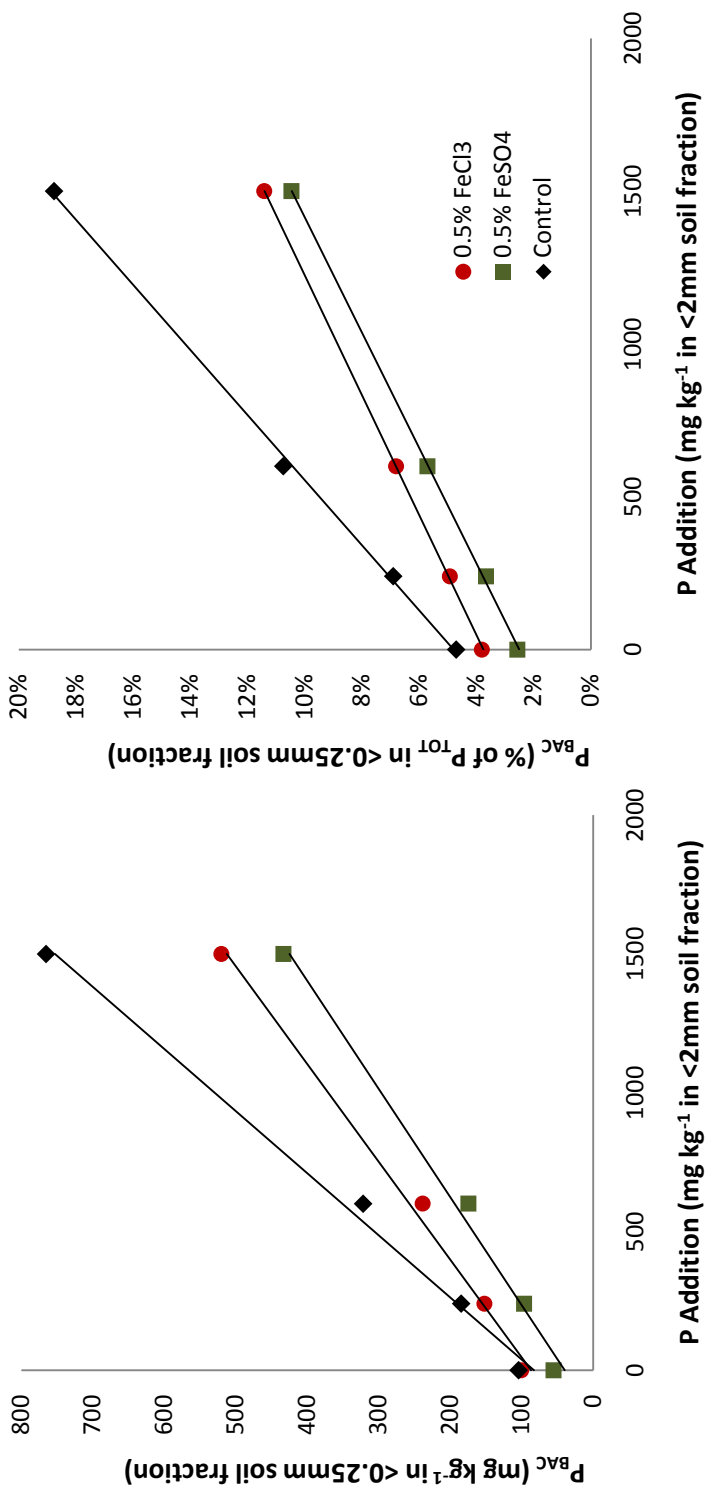


Figure 3.4 XAFS radial structure functions. Raw data are solid lines, experimental fitted data are red circles. No difference is observed in As bonding between FeCl₃-treated and control soils. Data and analysis by K. Scheckel, USEPA



Figures 3.5a,b Phosphate amendments dosing result in a linear increase bioaccessible arsenic in both Fe amended and control (un-amended) soils. Application of P-based fertilizers could potentially release As to soil solution, or reduce As bioavailability.



Figures 3.6a,b Much of the phosphate introduced to test soils is extracted during the SBRC-g in vitro bioaccessibility test. In control soils, nearly 20% of added P is bioaccessible. Duplicate analysis of P_{BAC} for one sample showed relative percent difference of 1.1%.

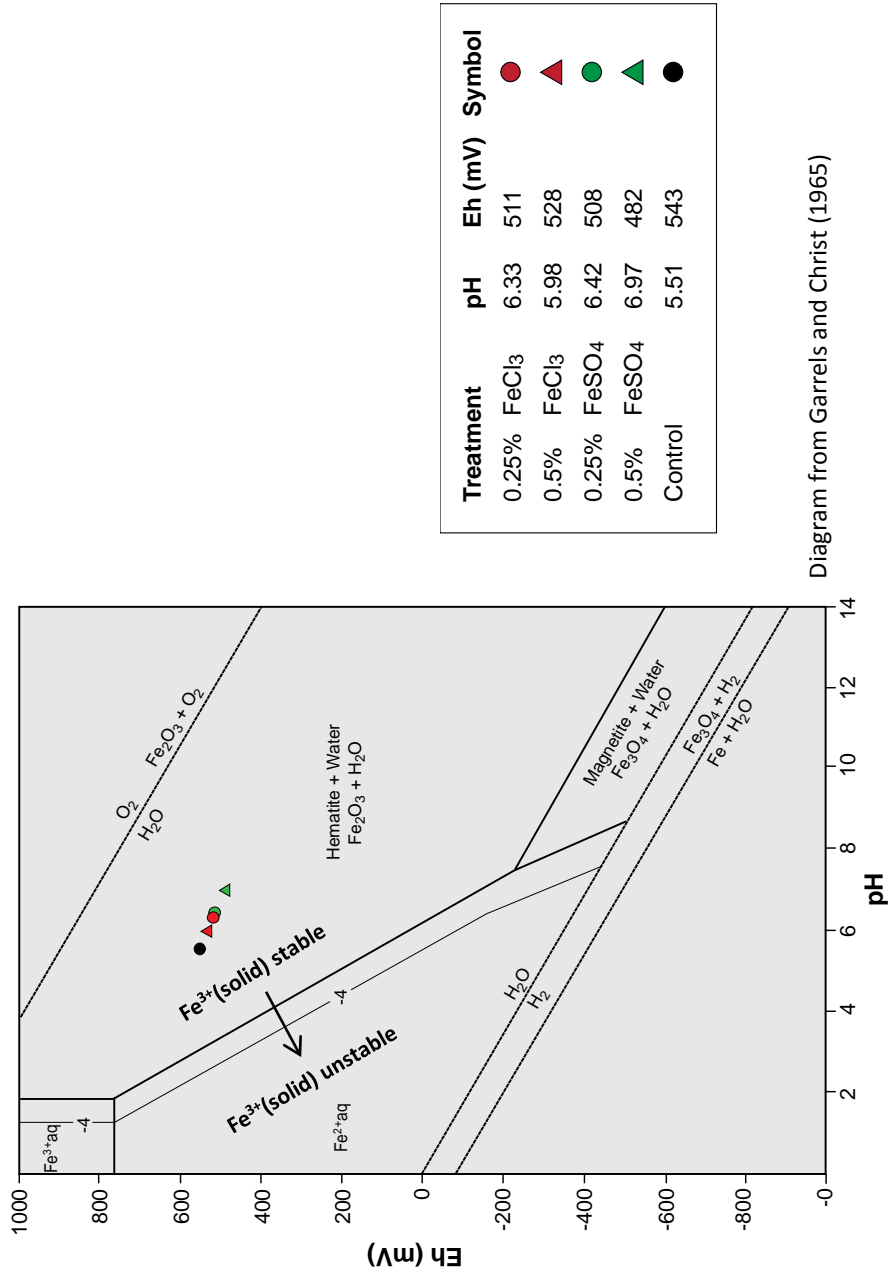


Diagram from Garrels and Christ (1965)

Figures 3.7 Eh-pH diagram of common Fe oxides, with test plot soils (336 d post treatment). Both treated and untreated soils are in geochemical field of stable Fe⁺³ solid phases. Lower pH or Eh (redox) conditions could potentially drive soils into unstable field, where Fe⁺³ solids are dissolved, releasing adsorbed As. The most likely situation that might lower Eh is extended flooding of soils.