

**EFFECTS OF LAND USE ON THE SPATIAL AND VERTICAL  
DISTRIBUTION OF ARSENIC IN SOIL CORES ON O'AHU**

**A THESIS SUBMITTED TO THE GLOBAL ENVIRONMENTAL SCIENCE  
UNDERGRADUATE DIVISION IN PARTIAL FULFILLMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF**

**BACHELOR OF SCIENCE**

**IN**

**GLOBAL ENVIRONMENTAL SCIENCE**

**By  
Sara Thomas**

**Thesis advisor  
Eric Heinen DeCarlo**

**December 2009**

I certify that I have read this thesis and that, in my opinion, is satisfactory in scope and quality as a thesis for the degree of Bachelor of Science in Global Environmental Science.

THESIS ADVISOR

---

Eric Heinen DeCarlo  
Department of Oceanography

## **ACKNOWLEDGEMENTS**

I would like to thank Jane Schoonmaker and my advisor Eric Heinen DeCarlo for inspiring me to become a part of the Global Environmental Science degree program. DeCarlo's assistance and guidance throughout my research made my senior thesis project an enjoyable and invaluable learning experience. I would also like to thank Rene Tada for all the resources she has provided for the undergraduates. Additionally, my appreciation is extended to Kathy Kozuma, Chuck Fraley, Didier Dumas, Patrick Drupp, and the rest of the DeCarlo lab, who all played some integral part of my research experience.

## ABSTRACT

Soil cores were analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to determine the effects of land use on spatial and vertical distribution of arsenic (As) in soils around the island of O'ahu, Hawai'i. Six cores were collected and divided into 10 cm increments at five locations. Two cores were obtained from a gardenia farm (WK1 and WK3) and one in a forested region of Manoa Valley (WK2), one from the Lyon Arboretum (LA), and two from fallow pineapple and sugarcane fields in Kunia (KU) and Waipahu (WAI), respectively.

Concentrations of As were above 500 ppm in all three of the cores taken along the Waieakua Stream in Manoa. The concentrations are consistent with the hypothesis that As is introduced to soils through anthropogenic activity, either the application of superphosphate fertilizers or pesticides. High concentrations in the forested area suggest prior human activity in Manoa Valley has left soils with elevated concentrations of As. Relatively low, yet still elevated over natural, concentrations of As measured in the WAI core suggest alternative methods of pest and weed control were applied to sugarcane crops in this field. Both the LA and KU core demonstrated concentrations of As similar to Hawaiian background levels.

In cores with As contamination, concentrations decrease as a function of depth but maximum concentrations in the soil column occur at 10-20 cm depth. Drastic decreases in concentrations of As below this depth may be due to the strong affinity of As to iron oxides ( $\text{FeO}_x$ ) in soils at the surface where As is introduced through anthropogenic activity. Tilling of surface soils or the uptake of As from surface soils by plants may account for the observed subsurface peak in concentration of As.

## TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	iii
ABSTRACT.....	iv
GOALS AND OBJECTIVES.....	1
1. INTRODUCTION.....	5
1.1. Hawai'i and O'ahu setting.....	5
1.2. Arsenic.....	6
General.....	6
In the environment.....	7
Toxicity.....	8
Groundwater contamination.....	9
Health consequences.....	10
2. BACKGROUND.....	11
2.1. Natural and anthropogenic occurrences of arsenic.....	11
2.2. Distribution across the United States and Hawai'i.....	13
2.3. Bioaccumulation.....	15
2.4.1 Remediation of As contaminated soils.....	15
<i>Phytoremediation</i> .....	15
<i>Pteris vittata</i> .....	16
Iron oxide and the inhibition of hyperaccumulation.....	17
2.4.2 As uptake by plants.....	18
Arsenate vs. arsenite uptake.....	19
Roots to shoots ratio.....	19
Phosphate versus arsenate uptake.....	20
3. METHODS.....	21
3.1.1 Soils.....	21
Preliminary Sample Collection.....	21
3.1.2. Field collection of soil cores.....	23
Lab preparation.....	25
Acid digestion and solubilization.....	25
3.2. Ferns.....	26
Fern collection and planting.....	26
Lab preparation.....	27
3.3. Inductively Coupled Plasma Mass Spectrometry.....	27
Quality assurance/ calibration.....	28
Calculations.....	28
4. RESULTS.....	30
4.1. Preliminary surface soils.....	30
4.2. Soil cores.....	30
Quality control of ICP-MS.....	36
4.3. Fern Material.....	37
5. DISCUSSION.....	38
5.1. General overview of all cores.....	38
5.2. Spatial and vertical distributions of As.....	38

Cores collected from Waikeakua gardenia farm and forested area along Waikeaku Stream.....	38
Fallow agricultural fields of Kunia and Waipahu.....	42
Island of Hawai'i comparison to KU and WAI cores and decline agriculture.....	43
Lyon Arboretum.....	45
5.3. Fundamental chemistry.....	45
5.5. Peak As concentrations in subsurface interval of cores.....	46
6. CONCLUSIONS.....	49
APPENDIX I.....	51
APPENDIX II.....	52
APPENDIX III.....	56
APPENDIX IV.....	58

## LIST OF FIGURES

### Figure

1. Map of O'ahu showing As concentrations at each sample location in the study of deGalleke, 2007.....	2
2. Annual rainfall intensities in cm on O'ahu influenced by prevailing trade winds. A site location map of Hawaiian Island chain is also shown.....	6
3. Eh-pH diagram for As at 25°C and 1 atmosphere.....	8
4. Arsenic concentrations (ppm) in the lithosphere and extraterrestrial objects.....	11
5. United States Geological Survey map of As concentration in groundwater in ppm across all states.....	14
6. Specific adsorption of phosphate, or arsenate, by iron oxides.....	17
7. Google image with view of surface soil sites relative to Manoa Valley.....	21
8. Google images of close up of surface soil sites.....	22
9. Google image of the location of soil cores gathered around O'ahu.....	24
10. Google image of the core sampling sites in Manoa Valley.....	24
11. Preliminary surface soil As concentrations.....	30
12. Arsenic concentrations in the WK1 core.....	32
13. Arsenic concentrations in the WK2 core.....	33
14. Arsenic concentrations in the WK3 core.....	34
15. Arsenic concentrations in the LA core.....	35
16. Arsenic concentrations in the KU core.....	35
17. Arsenic concentrations in the WAI core.....	36
18. Hawaiian sugarcane production from 1837-2006.....	43

## LIST OF TABLES

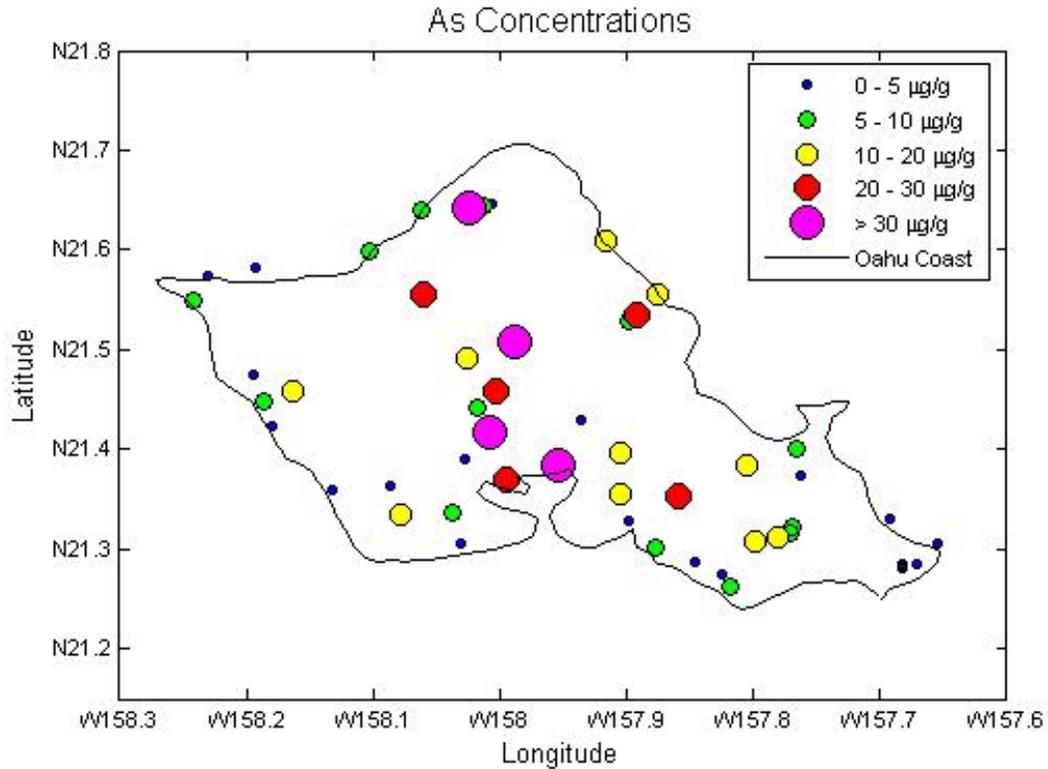
### Table

1. Sediment and tissue concentrations of As from Meador et al., 2004.....15
2. Arsenic concentrations for all soil cores.....31

## GOALS AND OBJECTIVES

Historical agricultural practices (e.g. application of pesticides and fertilizers which contain arsenic) in Hawai'i may have resulted in elevated concentrations of arsenic (As) in soils on the island of O'ahu. This study aims to investigate how land use affects the spatial distribution of As in soils across the island as well as how concentrations of As vary vertically in soil cores. Arsenic has previously been found in or near agricultural areas (DeCarlo et al., 2004; deGelleke, 2007), but the vertical distribution of As in the soil column remains unknown. Data from cores collected from agricultural areas may potentially enhance our understanding of how processes mobilize or bind As to particulate phases.

An initial investigation of the spatial distribution of As on the island of O'ahu was conducted by an undergraduate Global Environmental Science student, Laura deGelleke, at the University of Hawai'i at Manoa in 2007. Her collection of subsurface soil samples from various locations around the O'ahu revealed concentrations of As ranging from near zero to ~60 ppm, with highest concentrations occurring in urban parks or agricultural lands (Figure 1). Because sampling only collected soil below root structures or surface debris, deGelleke's results may not have been representative of true surface soil concentrations of As. This study will take into consideration the work of deGelleke for the spatial distribution of As on the island of O'ahu.



**Figure 1** Map of O'ahu showing As concentrations at each sample location in the study of deGelleke, 2007.

Ma et al. (2001) demonstrated that the fern species *Pteris vittata* can hyperaccumulate As from contaminated soils. This study, conducted in Florida, demonstrated the ability of the *Pteris vittata* to serve as a method of phytoremediation of soils contaminated with As. Several other fern species including *Nephrolepis exaltata* have since been found to extract As from contaminated soils although none as efficiently as the *Pteris vittata* (Ma et al., 2001; Wang et al., 2002; Srivastava et al., 2005; Srivastava et al., 2006; Tu and Ma, 2004). The composition of soil in Hawai'i is different from that found in Florida, and it is unknown if soil properties are an important variable in the extent of As accumulation by plants capable of hyperaccumulation. The findings of Ma have inspired this study to investigate potential phytoremediation of As contaminated soils in the subtropical setting of Hawai'i.

The primary objective of this study is to expand on the findings of deGelleke (2007) and Ma et al. (2001) through the following goals:

- 1) To investigate the effects of land use (specifically agricultural activity) on concentrations of As in soils.
- 2) To determine the vertical distribution of As concentrations within soil cores.
- 3) To evaluate the fern species *Pteris vittata* and *Nephrolepis exaltata* with respect to their ability to accumulate As in biomass from contaminated Hawaiian soils.

This study is driven by the following null hypotheses:

- 1) Land use will have no effect on the concentration of As found in soils.
- 2) The distribution of As will be uniform within the vertical soil column.
- 3) The fern species *Pteris vittata* and *Nephrolepis exaltata* will demonstrate the same ability to accumulate As from Hawaiian soils as from Florida soils.

This study is expected to disprove the null hypotheses. The following working hypotheses are proposed for this investigation:

- 1) Agricultural application of superphosphate fertilizers will significantly elevate concentrations of As in soils compared to natural background levels in Hawai'i. This hypothesis was formed considering the results provided by deGelleke (2007), which demonstrated that highest concentrations of As were found in central O'ahu, where agricultural activity has existed historically. The study by deGelleke did not, however, confirm fertilizers as the source of As.
- 2) The geochemical behavior of As and the immediate addition of fertilizer to surface soils will influence As distribution in soil cores. Concentrations of As will decrease with increasing depth in soil cores obtained from agricultural fields. Because arsenate is a chemical analog to phosphate, the affinity of As to iron

oxides will elevate concentrations in near surface intervals where anthropogenic activity directly influences the soil.

3) Uptake of As by the fern species *Pteris vittata* and *Nephrolepis exaltata* will be inhibited due to the strong affinity of As to the iron oxides characteristic of Hawaiian soils.

# 1. INTRODUCTION

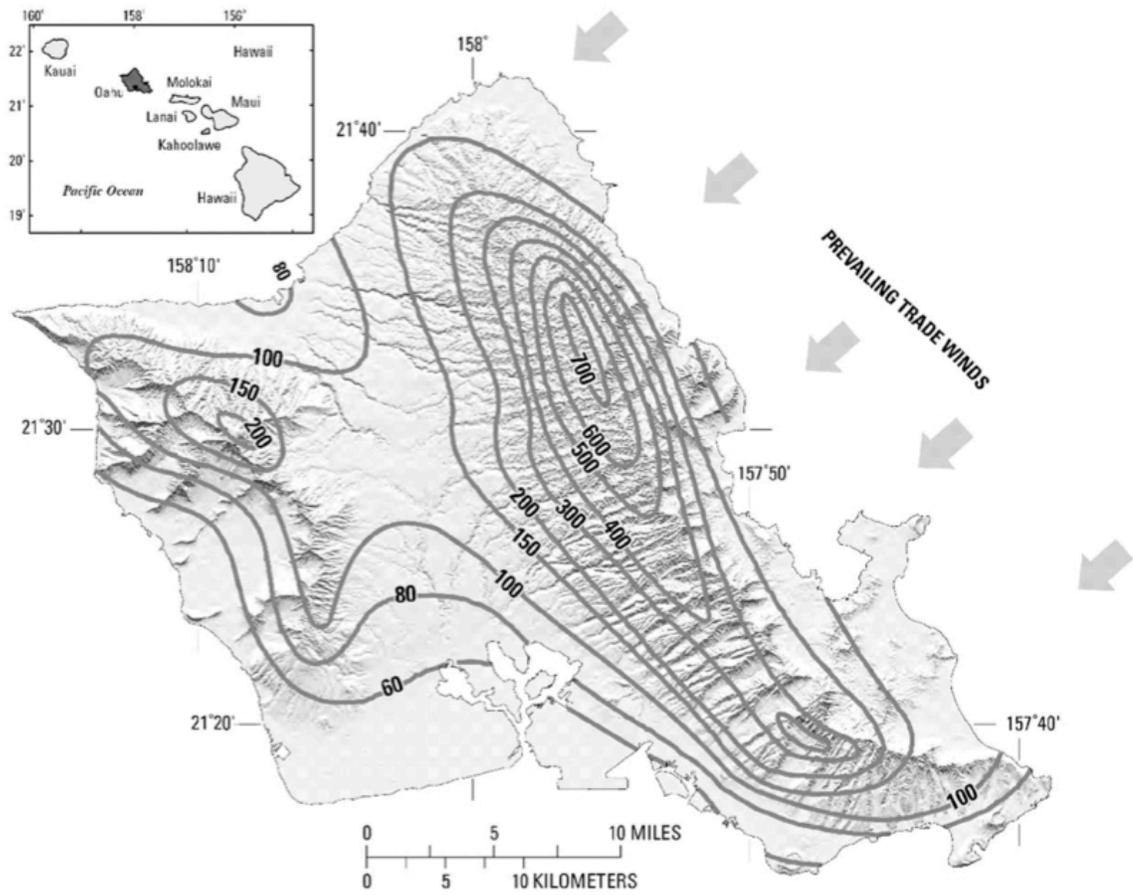
## 1.1. Hawai'i and O'ahu setting

The Hawaiian archipelago is the youngest part of the Hawaiian Ridge-Emperor Seamount chain. The entire chain stretches from the Big Island of Hawai'i to the Aleutian Trench near Alaska having formed from the movement of the Pacific Plate over the Hawaiian mantle hotspot (MacDonald et al., 1983). The eight principle islands, from oldest to youngest, Ni'ihau, Kaua'i, O'ahu, Moloka'i, Lana'i, Maui, Kaho'olawe, and Hawai'i comprise the main Hawaiian Island chain.

O'ahu is the third largest island with an area of 1546 km<sup>2</sup> and derives its shape from two shield volcanoes, the older Wai'anae and younger Ko'olau. Erosion, slope failure, and weathering over the course of several million years have left dramatically steep mountain slopes and deep valleys on the island. The Wai'anae mountain range peaks at 1207 m and the Ko'olau range at 931 m. Elevations of these mountains sharply drop off to near sea level over distances of only a few kilometers (DeCarlo et al., 2005).

Northeast trade winds have a dramatic impact on the island's climate. The winds are typically persistent throughout the year and bring warm, moist air across the Pacific Ocean. Air blown by the wind is forced to cool adiabatically once it collides with the windward Ko'olau mountain range. Moisture condenses and precipitates on the east side of the island, allowing warmer, dry air to sweep across the leeward side. Rainfall is greatest on the Ko'olau ridge, reaching approximately 700 cm annually (Giambelluca et al., 1984). The leeward side of O'ahu is drastically drier, with coastal areas receiving

less than 60 cm annually (Giambelluca et al., 1984). Contours of annual rainfall rates in cm for the island of O'ahu can be seen in Figure 2.



**Figure 2** Annual rainfall intensities in cm on O'ahu influenced by prevailing trade winds. A site location map of the Hawaiian Island chain is shown in the upper left corner. (Giambelluca et al., 1984 as cited by DeCarlo and et al., 2005)

## 1.2. Arsenic

### *General*

Arsenic is the 47<sup>th</sup> most abundant of the 91 naturally occurring elements. It appears on the periodic table in group 5A, immediately below phosphorus, with an atomic number of 33 and an atomic mass of 74.92. Arsenic may be present in either

organic or inorganic forms (Tu and Ma, 2004). and is mainly associated with chalcophilic, or sulfide minerals (Matschullat, 2000). Important mixed sulfides that carry As include gersdorffite (NiAsS), cobaltite (CoAsS), and arsenopyrite (FeAsS) (Matschullat, 2000). The penta-valent arsenate ( $\text{AsO}_4^{3-}$ ) shows many similarities to phosphate ( $\text{PO}_4^{3-}$ ) due to similar ionic radii (Goldschmidt, 1958 as cited by Matschullat, 2000), coordination with oxygen, and crystal-chemical relations (Matschullat, 2000). Because of these similarities  $\text{AsO}_4^{3-}$  qualifies as a chemical analogue to  $\text{PO}_4^{3-}$  (Tu and Ma, 2004).

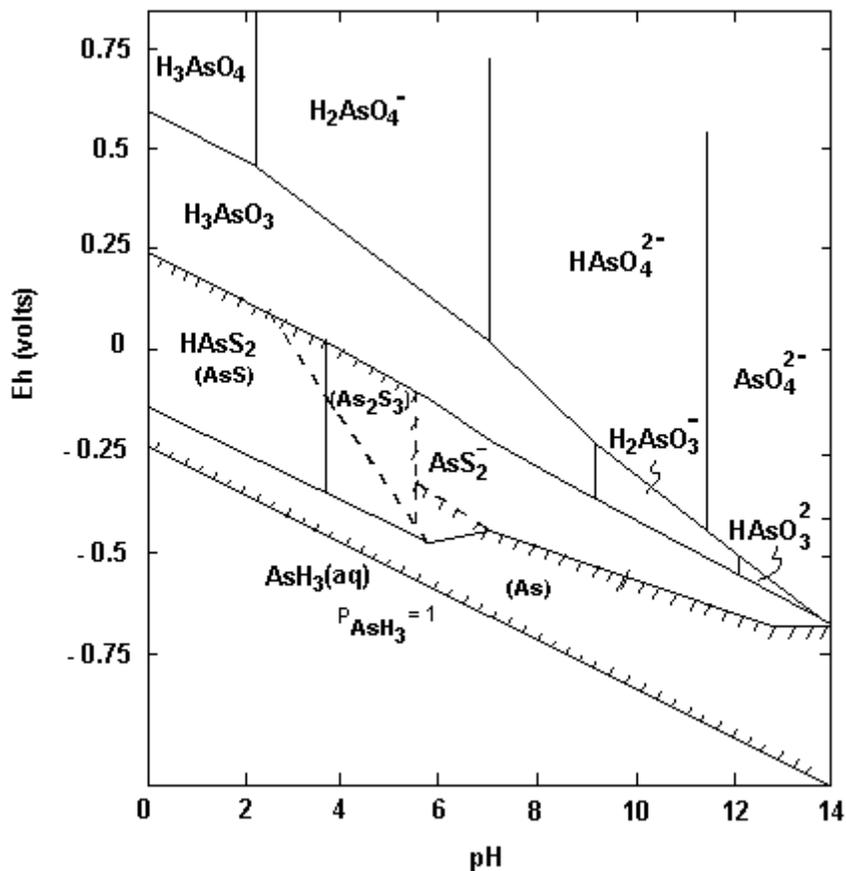
### ***In the environment***

Arsenic is ubiquitous in the environment, although its concentration is highly variable. While it ranks 20<sup>th</sup> in abundance in the earth's crust (Cullen and Reimer, 1989), it only comprises 0.0001% of it (Nriagu, 2002 as cited by Srivastava et al., 2005).

Arsenic has a strong affinity for pyrite (Nordstrom, 2002) and is often associated with sulfidic ores, sulfur-bearing mineral deposits, and metal ores (Cullen and Reimer, 1989; Nordstrom, 2002; Srivastava et al., 2005). It is coupled with igneous and sedimentary rocks (Cullen and Reimer, 1989), although As is found through a wide range of other media in the environment, including the atmosphere, aquatic systems, soils and sediments, and even organisms (Cullen and Reimer, 1989). Among the various media in which As is present, the second highest concentration of As in the lithosphere is found in phosphates at 12 ppm, following closely behind shales and/or schists with 13 ppm (Matschullat, 2000).

Arsenic occurs in the environment with oxidation states of -3, 0, +3, and +5 (Matschullat, 2000; Tu and Ma, 2004) depending on pH (Figure 3). In oxidized

environments inorganic As is generally present as arsenate ( $\text{AsO}_4^{3-}$ ). Arsenite ( $\text{AsO}_3^{3-}$ ) is the dominant form of As under anoxic/anaerobic conditions (Cullen and Reimer, 1989; Smith et al., 1998 as cited by Wang et al. 2002). In aerobic soils the dominant species of As is  $\text{AsO}_4^{3-}$  (Cullen and Reimer, 1989; Smith et al., 1998 as cited by Wang et al., 2002; Tu and Ma, 2004) which binds with clay minerals, organic substances, and iron oxides (Meador et al., 2003; Tu and Ma, 2004).



**Figure 3** Eh-pH diagram for As at 25 °C and 1 atmosphere (<http://www.inchem.org/documents/ehc/ehc/v224eh09.gif>)

### ***Toxicity***

Arsenic has been notorious for its toxicity throughout history. It is potentially the most influential element of human history because of its poisoning capabilities, first

believed to have caused the death of the god Hephaestus (Nriagu, 2002). Many murderers during Imperial Rome used As to poison their victims (Vaugh, 2006) and history has documented the killing and terrorizing of many aristocrats and noble gentlemen through As intoxication (Nriagu, 2002). Arsenic has also been widely used historically by women to free themselves from abusive husbands and undesired pursuers (Nriagu, 2002). Arsenic toxicity was also documented by lung cancer rates that were notably elevated among miners who inhaled As in the late 1800's (Smith et al., 2002).

### ***Groundwater contamination***

Elevated concentrations of As in soils pose a threat to human health because under the appropriate conditions arsenic may leach from soils and contaminate groundwater resources. High concentrations of dissolved As have been found to be caused by oxidation and dissolution of arsenian pyrite ( $\text{Fe}(\text{As}, \text{S})_2$ ) and arsenopyrite ( $\text{FeAsS}$ ) in various locations across the globe (Welch et al., 2000 as cited by Nordstrom, 2002). Perhaps the most striking cases of As poisoning from groundwater contamination were witnessed in various districts of Bangladesh and West Bengal, India, where a combined 120 million people were subjected to water containing concentrations of As over the World Health Organization (WHO) limit of 50 ppb (Uttam et al., 2000). Thirty-six million people in the Bengal Delta remain at risk according to Nordstrom (2002). Other cases of As contaminated groundwater have occurred in approximately 20 locations worldwide, including Inner Mongolia, China, and Taiwan (Uttam et al., 2000; Nordstrom, 2002), Chile, Argentina, and Mexico (Nordstrom, 2002) and Vietnam (Berg et al., 2001). To limit As exposure in the United States, the Environmental Protection Agency (EPA) reduced the permissible level of As in drinking water from 50 ppb to 10

ppb in 2002 (Smith et al., 2002). Because elevated concentrations of As in soils have been known to pose a risk to human health, remediation of contaminated sites is important.

### ***Health consequences***

Arsenic poisoning leads to severe health consequences. Several different arsenical skin lesions including diffuse melanosis (throughout the entire body or palms of the hands), spotted melanosis, leucomelanosis (adjacent white and black spots), and buccal mucus membrane melanosis (on tongue, gums, and lips) were noted as As toxicity symptoms in India (Uttam et al., 2000). Severe poisoning has been known to cause enlargement of the spleen and liver as well as fluid in the abdomen (Uttam et al., 2000). Internal cancers of the lung and urinary tract were observed in Argentinians who drank water contaminated with As (Bergoglio, 1964 and Biagini, 1966 as cited by Smith et al., 2002), and mortality rates associated with As poisoning in Taiwan during 1985 were due to lung, bladder, and kidney cancers (Chen et al., 1985 as cited by Smith et al., 2002).

## 2. BACKGROUND

### 2.1. Natural and anthropogenic occurrences of arsenic

Both natural and anthropogenic sources contribute to the presence of As in the environment (Wang et al., 2002). Arsenic occurs naturally in the universe (Figure 4) and in earth's crust (Mrittanjai et al., 2005) and is released through volcanic eruptions and hydrothermal activity (Matchullat, 2000).

Medium	Concentration	Source <sup>a</sup>
Universe	0.008 (ppm)	Winter (1998)
Sun	0.004 (ppm)	Winter (1998)
Stony meteorites	1.8	Onishi (1969), Winter (1998)
Iron meteorites	11	Onishi (1969), Winter (1998)
Earth crust, total <sup>b</sup>	1.0; 1.7; 1.8	Taylor and McLennan (1995), Wedepohl (1995), Lide (1996)
Upper crust	1.5; 2.0	Taylor and McLennan (1995); Wedepohl (1995)
Ultramafic rocks	0.7	Koljonen (1992)
Ocean ridge basalts (MORB)	1.0	Koljonen (1992)
Gabbros; basalts	0.7	Koljonen (1992)
Granites; granodiorites	3.0	Koljonen (1992)
Sandstones	0.5; 1.0	Onishi (1969); Koljonen (1992)
Shales; schists	13	Onishi (1969); Koljonen (1992)
Carbonates	1.0; 1.5	Onishi (1969); Koljonen (1992) Chester (1993)
Phosphates	12	Onishi (1969)
Metamorphites	0.5–11	Onishi (1969)
Coal	0.34–130; 5–45; 1–10.000;	Piver (1983), Pacyna (1987) Onishi (1969)
Crude oil	0.0024–1.63; 0.134; 0.005–0.14	Pacyna (1987); Piver (1983); Veal (1966) in Onishi (1969)

<sup>a</sup> Koljonen (1992), Taylor and McLennan (1995), Lide (1996) in Reimann and Caritat (1998).

<sup>b</sup> Mass of the earth crust:  $2.13 \times 10^{19}$  t; Mass of the upper crust:  $1.13 \times 10^{19}$  t (after Wedepohl, 1995).

**Figure 4** Arsenic concentration (ppm) in the lithosphere and extraterrestrial objects. (Matschullat et al., 2000)

The relative abundance of As varies depending on the geologic history of a location, but the weathering of As-containing rocks may be the dominant mechanism that mobilizes As to an environment (Tamaki and Frankenberger, 1992 as cited by deGelleke, 2007).

The concentration of As in the environment is also elevated through various anthropogenic activities. These include many high temperature combustion processes, such as oil and coal fired power plants, waste incineration, and cement works. Industrial inputs from ore production and processing, electronics, metal treatment, galvanizing,

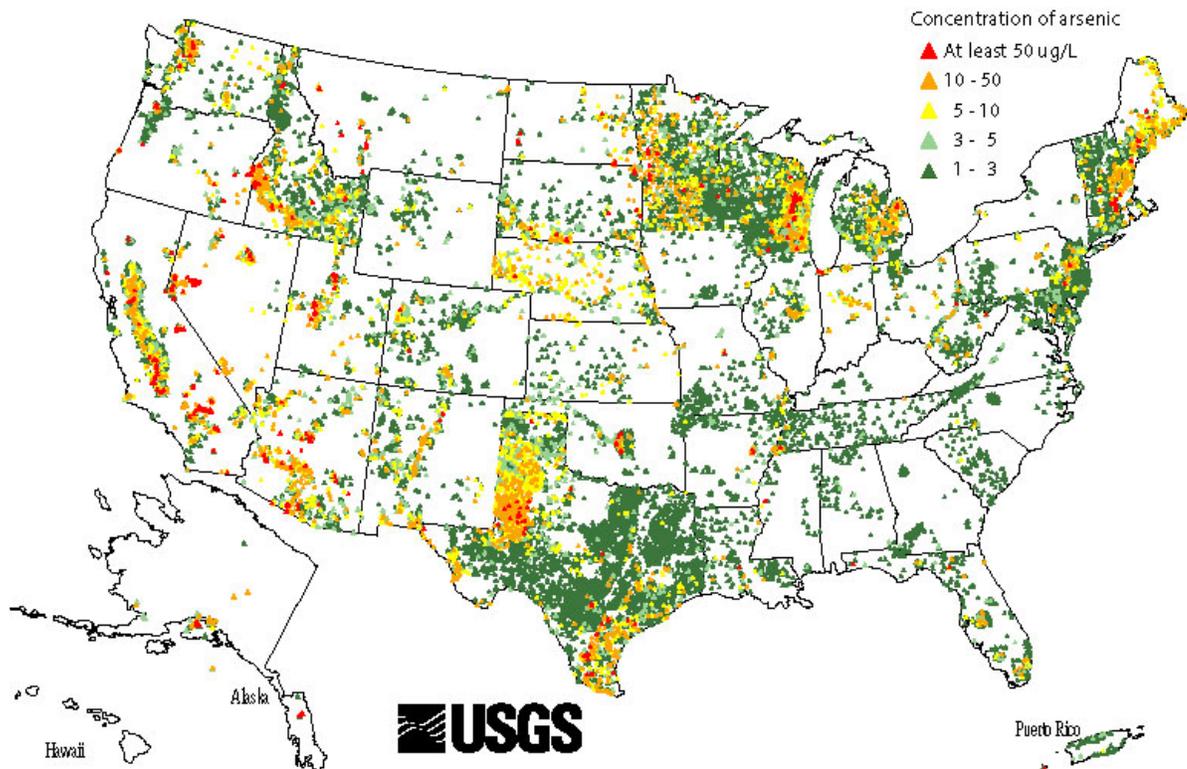
ammunition factories, glassware production and wood preservative (Savory and Wills, 1984 as cited by Matschullat, 2000) as copper-chromated arsenate (CCA) are also anthropogenic sources of As to the environment. Roughly 90% of As used for industrial purposes in the United States is used as a wood preservative (US EPA, 2000). Arsenic is also introduced to the environment through mineral extractions and the processing of wastes, poultry, and swine feed additives (Nordstrom, 2002).

Additionally, As concentrations in soils can be elevated through agricultural activity (Charter et al., 1995; Campos, 2002; Yokel and Delistraty, 2003; Cutler et al., 2006). Arsenic may be introduced to the environment along with phosphorus (P) compounds or through the use of pesticides and fertilizers (Campos, 2002). Pesticides have been documented to contain As in the chemical compound of lead arsenate ( $\text{PbHAsO}_4$ ) (Yokel and Delistraty, 2003) or sodium arsenate ( $\text{NaH}_2\text{AsO}_4$ ) (Cutler et al., 2006). Fertilizers used on crops introduce large quantities of P, an essential plant nutrient, to soils as  $\text{PO}_4^{3-}$ , which is readily available for plant uptake. Superphosphate fertilizers, however, may also contain As because its anion  $\text{AsO}_4^{3-}$  is iso-structural to  $\text{PO}_4^{3-}$  and chemically similar. Because iron rich soils (latosols) convert  $\text{PO}_4^{3-}$  into insoluble forms and decrease its availability as a nutrient (Campos, 2002), superphosphate fertilizers are often used in agricultural settings to increase the availability of this essential plant nutrient. Elevated levels of  $\text{PO}_4^{3-}$ , however, are suspected of increasing the mobility and solubility of As in soils (Campos, 2002; Peryea and Kammereck, 1997). Furthermore, As has been documented as being present in fertilizers from several different producers. Fertilizers from companies such as Agrium US Inc., Belle Plaine Coop., Black Diamond Organics, Crop Production Services Inc.,

and Earthsoils contain concentrations of As < 41 ppm. Most shockingly, fertilizers produced by Ironite® contain concentrations of As in the range of 4,000 to 6,200 ppm. These fertilizers are made from mining wastes and contain As level several of orders of magnitude higher than any other fertilizers (EPA, 2002).

## **2.2. Distribution across the United States and Hawai'i**

The distribution of As in groundwater across the United States, like the rest of the world, lacks uniformity (Figure 5). The oxidation and potential iron reduction of arsenopyrite-rich zones occurring in igneous and metamorphic rocks near Fairbanks, Alaska create some of the highest natural dissolved As concentrations found in groundwater, ranging from 1-10 ppm (Muller et al., 2001 as cited by Nordstrom, 2002). The common range of As in water systems throughout the Midwest and New England is 0.002-0.01 ppm but western states display a larger number of water systems with As levels greater than 0.01 ppm (US EPA). Geothermal fluids produced by the Hawai'i Geothermal Project well-A (HGP-A) contained concentrations of the oxyanions of As(+3) and As(+5) in the range of 0.1 ppm (DeCarlo and Thomas, 1985).



**Figure 5** United States Geological Survey map of As concentrations in groundwater in  $\mu\text{g}$  per liter (ppm) across all states ([http://water.usgs.gov/nawqa/trace/pubs/geo\\_v46n11/fig1.html](http://water.usgs.gov/nawqa/trace/pubs/geo_v46n11/fig1.html))

Hawai'i's tropical climate allows year round agriculture and large-scale agriculture, in the form of pineapple and sugarcane plantations, was the first dominant industry for the state. Arsenic contamination of soils is common in many agricultural fields where pesticides and fertilizers were applied to crops. Natural concentrations of As in Hawaiian soils span between 2-20 ppm (DeCarlo et al., 2005; Cutler et al., 2006), but concentrations in the range of 1000 ppm have been found in sugar plantation soils in Ola'a Plantation near Hilo on the island of Hawai'i (Cutler et al., 2006).

### 2.3. Bioaccumulation

Arsenic toxicity is propagated through bioaccumulation. The mobility of As into water during the first flush effect of storm events may affect biota via bioaccumulation (Tinsley, 1979 as cited by DeCarlo et al., 2004). Work by Meador et al. (2003) demonstrated bioaccumulation of As in livers and stomachs of fish and invertebrate species in various California and Alaska sites where sediments contained As (Table 1).

Site	Sediment	Liver	Muscle	Gill	Stomach	TOC (%)	AVS	% fine sed
<b>Alaska</b>								
Lutak	6.2 (0.3)	38.3 (22.5)	28.5 (12.5)	na	8.7 (1.1)	0.76 (0.02)	0.2 (0.06)	89 (12)
Olsen Bay	8.5	26.8 (9.6)	33.9 (3.8)	na	10.9 (1.3)	2.2	0.5	na
Port Valdez	22.3 (2.0)	290 (193)	52.3 (26.9)	na	40.4	0.62 (0.05)	0.01 (0.02)	98 (1)
Skagway	1.7 (0.9)	102 (137)	20.7 (14.8)	na	9.4 (2.3)	0.24 (0.11)	0.04 (0.04)	62 (35)
<b>California</b>								
Bodega Bay	4.8 (0.1)	19.4 (1.9)	8.5 (3.8)	3.3 (1.0)	45.4 (16.5)	0.23 (0.07)	1.0 (1.3)	8 (3)
Hunters Pt. 92	9.7 (1.0)	5.5 (0.7)	5.3 (2.8)	na	2.8 (0.4)	1.3 (0.05)	6.0 (3.6)	70 (34)
Hunters Pt. 93	8.4 (0.2)	6.5 (1.1)	3.5 (0.9)	1.5 (0.1)	5.4 (2.4)	1.1 (0.09)	5.6 (5.1)	70 (34)
Long Beach	10.4 (0.7)	5.7 (1.0)	4.3 (0.8)	na	15.6 (5.9)	1.5 (0.02)	5.3 (1.2)	91 (1)
Monterey	3.9 (0.8)	40.5 (6.6)	45.6 (23.8)	3.4 (0.7)	13.4 (3.2)	0.13 (0.02)	0.09 (0.02)	10 (5)
Moss Landing	4.6 (0.8)	na	na	na	na	0.14 (0.07)	1.0 (1.4)	20 (21)
Oakland	8.9 (1.1)	8.2 (1.0)	5.7 (0.8)	1.4 (0.2)	9.3 (5.5)	0.83 (0.44)	2.5 (1.9)	91 (1)

*Note.* All values are mean, with standard deviation in parentheses. Concentrations as  $\mu\text{g/g}$  dry wt. Total organic carbon in sediment (TOC) as percentage dry weight. Acid volatile sulfides (AVS) as  $\mu\text{mol S/g}$  dry weight.  $n = 3$  composite samples per site. Each fish composite contained three individuals. Each sediment composite contained sediment from three separate grab samples. % fine sed is the percentage of sediment particles  $<63 \mu\text{m}$ , which equals the division between sand and silt + clay. na, not analyzed. % fine sed was determined for these sites during previous sampling (see Meador *et al.* 1994).

**Table 1** Sediment and tissue concentrations of As. (Meador et al., 2004).

Arsenobetaine, an organic As compound, is the main chemical species of As in fish tissues (Shiomi et al., 1995; Wrobel et al., 2002). Organic forms of As have lower toxicity than inorganic forms, but both ultimately pose a risk to human health if contaminated fish are made available for consumption.

### 2.4.1 Remediation of As contaminated soils

#### *Phytoremediation*

Because elevated As concentrations in soils represent a continued toxicity risk, the development of methods to remediate contaminated soils and sediments has become a

topic of high interest. Phytoremediation, the treatment of environmental problems via plants, is of particular interest because it can potentially eliminate the need to dispose of the contaminant material elsewhere. Several studies have shown fern species capable of extracting As from contaminated soils (Ma et al., 2001; Wang et al., 2002; Srivastava et al., 2005; Srivastava et al., 2006; Tu and Ma 2004). The *Pteris vittata* (Chinese brake fern) has demonstrated exceptional ability to hyperaccumulate As from soils (Ma et al., 2001; Wang et al., 2002; Srivastava et al., 2005; Tu and Ma, 2004) while the species *Nephrolepis exaltata* (Boston fern) is also capable of accumulating As (Srivastava et al., 2005; Tu and Ma, 2004).

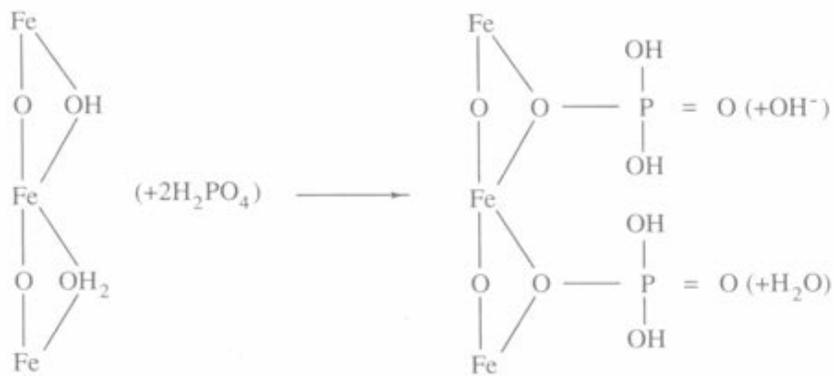
### ***Pteris vittata***

The *Pteris vittata* was the first fern discovered to hyperaccumulate As (Ma et al., 2001). Various experiments show it to be the most effective fern species for phytoremediation of contaminated sites (Tu and Ma, 2004; Ma et al., 2001; Wang et al., 2002; Srivastava et al., 2005). The *Pteris vittata* was not only found to efficiently extract As from contaminated soils but also to accumulate 755 ppm As when growing in soils containing only 6 ppm As over a 2 week period (Ma et al., 2001). The fern's ability to accumulate large amounts of As from uncontaminated soils indicates an efficient As uptake and translocation system (Tu and Ma, 2004). An uptake kinetics study by Wang et al. (2002) on the *Pteris vittata* showed it has three key features that are characteristic of metal/metalloid hyperaccumulator plants. These include an effective root uptake, efficient root to shoot translocation, and a tolerance to As within plant cells. The *Pteris vittata* also shows an effective detoxification mechanism towards As (Tu and Ma, 2004). The detoxification of  $\text{AsO}_4^{3-}$  occurs within the plant cells, where it is reduced to  $\text{AsO}_3^{3-}$

(Pickering et al., 2000, Schmöger et al., 2000, Hartley-Whitaker et al., 2001 as cited by Wang et al., 2002). The combination of these traits makes the *Pteris vittata* extremely efficient at accumulating As from both contaminated and uncontaminated soils.

***Iron oxide and the inhibition of hyperaccumulation***

Various studies on the mainland, specifically Florida, have shown the *Pteris vittata* species suitable for phytoremediation of As contaminated soils (Tu et al., 2004; Srivastava et al., 2005; Wang et al., 2002; Ma et al., 2001; Tu and Ma, 2004) and the *Nephrolepis exaltata* capable of some accumulation (Tu et al., 2004; Srivastava et al., 2005), but there is reason to believe that the soil composition of Hawai'i may inhibit the ability of these fern species to accumulate As from soils. The subtropical volcanic nature of Hawai'i creates iron oxide rich soils that differ considerably from the predominantly calcium carbonate or quartz and clay rich soils found in granite or sedimentary rock characteristic of Florida. The tendency of As to bind to iron oxides (Meador et al., 2005) may therefore prevent efficient uptake of As by these ferns in Hawaiian soils (Figure 6).



**Figure 6** Specific adsorption of phosphate by iron oxides may lead to the release of OH<sup>-</sup> or H<sub>2</sub>O (Binkley, 1986 as cited by Schlesinger). AsO<sub>4</sub><sup>3-</sup>, the chemical analog of PO<sub>4</sub><sup>3-</sup>, can substitute for PO<sub>4</sub><sup>3-</sup>.

#### 2.4.2 Arsenic uptake by plants

Because exposure to As can cause serious adverse health effects, there is much interest in remediation of contaminated sites. Fortunately, As occurs mainly as  $\text{AsO}_4^{3-}$  in aerobic soils (Smith et al., 1998 as cited by Wang et al., 2002; Tu and Ma, 2004), which may then be substituted chemically for  $\text{PO}_4^{3-}$  and be available for plant uptake (US EPA, 2000). Arsenate uptake by plants was demonstrated when Ma et al. (2001) discovered that ferns growing in soils contaminated with CCA contained significant quantities of As in their biomass. Specifically, the *Pteris vittata* accumulated As in the fronds up to 126-fold the concentration of As in the soil, making it the first known hyperaccumulator of arsenic (Ma et al., 2001). The term ‘hyperaccumulator’ was first applied to plant species that accumulated nickel but was later used to describe plants which attain metal concentrations > 1000 ppm (Reeves and Basker, 2000 as cited by Srivastava 2006). Hyperaccumulators are also described as plants that take up toxic elements and sequester high concentrations in their above ground parts (Tu and Ma, 2004). Since the 2001 Florida study by Ma, the *Pteris biaurite* L., *Pteris quadriaurita* Retz, *Pteris cretica*, and *Pteris ryukyuensis* Tagawa fern species have been identified as hyperaccumulators of As (Srivastava et al., 2006). The species *Nephrolepis exaltata* has also been found to accumulate As, although not well enough to qualify as a hyperaccumulator (Tu and Ma, 2004). The discovery of plants that hyperaccumulate As make phytoremediation of As contaminated sites possible.

### ***Arsenate vs. arsenite uptake***

Arsenic present in plant biomass is almost entirely in inorganic form (Ma et al., 2001; Wang et al., 2002) with some present as organoarsenic (Ma et al., 2001). Arsenic is taken up primarily as  $\text{AsO}_4^{3-}$  (Wang et al., 2002; Tu and Ma, 2004) although it may also be acquired as  $\text{AsO}_3^{3-}$  (Ma et al., 2001). As a chemical analog to  $\text{PO}_4^{3-}$ ,  $\text{AsO}_4^{3-}$  is taken up via the  $\text{PO}_4^{3-}$  transport systems in ferns (Asher and Reay, 1979, Lee, 1982, Ullrich-Eberius et al., 1989 and Meharg and Macnair, 1992 as cited by Wang et al., 2002). Phosphate carriers in the plasma membrane of cells mediate  $\text{AsO}_4^{3-}$  entry into the cytoplasm (Asher and Reay, 1979 and Meharg and MacNair, 1990 as cited by Tu and Ma, 2004). Arsenite, however, was not found to share the same transport system as  $\text{PO}_4^{3-}$  (Wang et al., 2002); this may be attributed to the need for  $\text{AsO}_3^{3-}$  to be oxidized to  $\text{AsO}_4^{3-}$  before plant uptake (Ma et al., 2001).

### ***Roots to shoots ratio***

The ratio of acquired As in the roots and shoots of the *Pteris vittata* is not unity. Arsenic in the shoots of the fern are significantly higher than in the roots (Ma et al., 2001; Wang et al., 2002; Tu and Ma, 2004; Srivastava et al., 2005). Wang et al. (2002) found the As concentration ratio between roots and shoots to range between 1.3 and 6.7. Ma et al. (2001) found 47-80%, with up to 93%, of the As concentrations occurring in the shoots with 8% in the roots. The ability to hyperaccumulate As in the above ground biomass of the plant efficiently removes the contaminant from the soils, which is an important objective of remediation of contaminated sites.

### ***Phosphate versus arsenate uptake***

The availability of  $\text{PO}_4^{3-}$  in the soil is thought to influence the rate of As accumulation. Increasing  $\text{PO}_4^{3-}$  concentrations in soils decreases the rate of  $\text{AsO}_4^{3-}$  uptake and the concentration of As in both the roots and shoots, with the effect significantly greater on the roots (Wang et al., 2002; Tu and Ma, 2004). Conversely, increasing the available  $\text{AsO}_4^{3-}$  in the soils significantly decreases the concentration of P in the roots (Wang et al., 2002). The concentration of phosphorus was found to be higher in roots than in the shoots, suggesting  $\text{PO}_4^{3-}$  does not compete with As in the transport from roots to shoots (Wang et al., 2002). If the *Pteris vittata* is grown in soils starved of P,  $\text{AsO}_4^{3-}$  sequestration in plant biomass increases by a factor of 2.5 (Tu and Ma, 2004). Anthropogenic addition of P via fertilizers therefore has an impact on the rate of As accumulation in plants.

### 3. METHODS

#### 3.1.1 Soils

##### *Preliminary Sample Collection*

Surface soil samples (0-20 cm) were gathered from two locations in Manoa Valley (Figure 7). One sample was collected in a gardenia farm, located upstream from the USGS Waikeakua Stream gage, and another from along the bank of Waihi Stream (Figure 8).



**Figure 7** View of surface soil sites relative to Manoa Valley



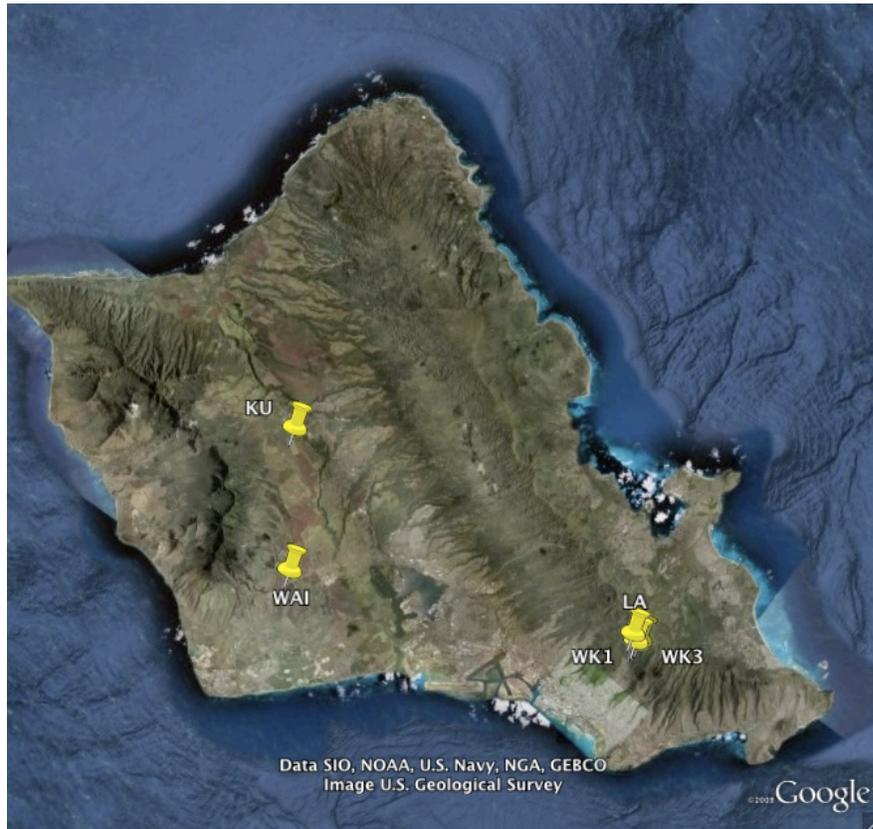
**Figure 8** Close up of surface soil sites

Sampling of the flower farm was inspired by the work of DeCarlo et al. (2004) who observed elevated concentrations of As in SPM in the Waikeakua Stream following the first flush of a storm event. Superphosphate fertilizers have been previously suspected of enhancing As concentrations in these soils (DeCarlo and Dollar, 1997 as cited by DeCarlo et al., 2004) and were thought to be the source of As to the Waikeakua Stream. Two subsamples were gathered from each site, the first subsample from 0-15 cm depth and the second from 15-20 cm depth. Soil was gathered with a posthole digger and collected into gallon-sized Ziploc® bags. Bags were labeled with the date, location, and soil depth, double bagged and brought back to the lab for processing and analysis. This initial collection of samples provided background information as to how As levels vary in

agricultural and non-agricultural areas. The results from the preliminary analysis of these samples were then used to develop hypotheses as to where As contaminated and non-contaminated surface soils might be found.

### **3.1.2. Field collection of soil cores**

Following the analysis of preliminary soil samples and the development of hypotheses, a plan was devised to collect soil cores from various environments with potential As contamination. In total six soil cores were collected from five sites on O'ahu, Hawai'i. Four cores were collected in Manoa Valley; two (WK1 and WK3) from the Waikeakua gardenia flower farm just upstream the USGS water gage on the Waikeakua Stream, one (WK2) from a forested area approximately 350 m up the Waikeakua Falls trail from the gardenia farm, and one from the Lyon Arboretum (LA). The remaining two cores were obtained in fallow agricultural fields; one from a Kunia pineapple field (KU) and the other from a sugarcane field off the H3 highway in Waipahu (WAI). More details of these sites are listed in Appendix 1 and locations are shown in Figures 9 and 10.



**Figure 9** Location of soils cores gathered around O'ahu



**Figure 10** Core sampling sites in Manoa Valley

Of the six cores collected, the WK1, WK3, KU and WAI locations were chosen because of obvious agricultural land use. The latter was implied to indicate frequent and long-term use of fertilizer and/or pesticides, which likely contained As. The WK2 and LA locations were selected as regions deemed to have experienced minimal anthropogenic influence.

Soil cores were collected with use of a posthole digger. Sections of each core were collected in approximately ten-centimeter depth intervals. Ziploc® bags were used to store the sections and labeled with the date, location, core number, and depth range before being double bagged and taken back to the laboratory for processing and analysis.

#### ***Lab preparation***

Sections of each core were dried to constant weight in a laboratory oven at 60°C to remove moisture. Large roots, rocks, leaf material, and other debris were removed from the soil prior to homogenizing. Sections of the dried cores were ground either by hand using a mortar and pestle or mechanically with a ball and mill grinder. Following homogenization approximately 100 mg subsamples of core intervals were weighed to the nearest 0.1 mg.

#### ***Acid digestion and solubilization***

Subsamples of all soil cores were digested and solubilized in a strong trace metal clean acid solution containing 4 ml nitric acid (HNO<sub>3</sub>), 2 ml hydrochloric (HCl), and 1 ml hydrofluoric (HF). Samples were digested in sealed Teflon vessels using a CEM MARS EXPRESS microwave system. Once digested, the acid mixture was evaporated to near

dryness in the same microwave system. The residue was then redissolved in 2% (V/V) trace metal clean HNO<sub>3</sub> and diluted by weight to approximately 100 g and weighed to the nearest 0.01 g. Each sample was further diluted 10 fold with 2% HNO<sub>3</sub> in preparation for analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). A standard reference material (MESS-1) and blanks were also carried through all digestion procedures for quality control. Details of the digestion procedure are given in Appendix II.

### **3.2. Ferns**

#### ***Fern collection and planting***

A total of 16 ferns were collected for this study. Ten ferns of the species *Nephrolepis exaltatta*, more commonly know as the Boston Fern, were purchased from Home Depot® between 11-12 September 2009. Eight of these ferns were planted in two Rubbermaid® action packers on 17 September 2009. Four ferns were placed in As-contaminated soil collected from the same area where cores WK1 and WK3 were obtained, and the remaining four in non-contaminated soil from the Waihi Stream bank. The remaining two ferns were brought to the lab to represent a control for the *Nephrolepis exaltatta*. Five *Pteris vittata* ferns were collected from the University of Hawai'i Campus near the Art Building on 17 September 2009, four of which were planted in two Rubbermaid® containers following the same planting pattern done for the *Nephrolepis exaltatta* species. An additional *Pteris vittata* plant was gathered on 26 October 2009 and brought to the laboratory to provide a total of two control plants for the species. Plants were grown in their respective soils for approximately nine weeks. Specific details on plants can be found in Appendix III.

### ***Lab preparation***

Plants were taken apart to separate the roots from the shoots. Plant material was rinsed free of dirt then cleaned further using an ultrasonic bath to ensure all soil particles were removed from both the fronds and roots. Roots and shoots were separately placed into a laboratory oven at 60°C and dried to a constant weight. Plants need to be homogenized and then digested in mineral acids. Trace metal clean conditions analogous to the soil digestion will be used to prepare the plant material for ICP-MS analysis.

### **3.3. Inductively Coupled Plasma Mass Spectrometry**

An ICP-MS was used to determine the concentrations of arsenic in the digested sample solutions. The fundamental principle of operation of the ICP-MS is to cause ionization of an analyte, creating positively charged ions, by use of a high temperature plasma discharge (Thomas, 2001a). The system operates by pumping a liquid sample into the sample introduction unit which is composed of two parts. The first is a nebulizer, which uses mechanical shear of a liquid by a gas flow to generate aerosols from the liquid sample. The fine spray is then passed through a spray chamber, which rejects larger aerosol droplets and only allows the finest droplets to be transported into the inductively coupled argon plasma (Thomas, 2001b). As an aerosol, the sample is guided to the base of the plasma by a quartz injector tip and passes through different heating zones of the plasma torch, which reaches 6,000-7,000 K in the analytical zone. The aerosols that travel through the plasma are desolvated, atomized then ionized. Samples exit the system as excited atoms and ions which provide a reliable representation of the elemental

composition of each subsample (Thomas, 2001a). A description of the method used in this work is provided by Wen et al. (1997) as described by DeCarlo et al. (2004).

***Quality assurance/ calibration***

Multi-element standards over a range of concentrations (0, 1, 2.5, 5, 10, 15, and 20 ppb) were used for instrument calibration. Signal intensities of internal standards selected to cover the entire analytical mass range were also used to correct for any instrument drift (DeCarlo et al., 2004). Arsenic concentrations were determined by monitoring the signal intensity at mass 75, the only isotope of As. The NRC Canada MESS-1 reference material and blanks were run roughly every eight samples to ensure quality control and accuracy. Each sample was measured in triplicate through the ICP-MS, and then averaged for reporting purposes. Other elements (Cd, Co, Cr, Cu, Ni, Pb, U and Zn) were also determined to examine any inter-element relationship that may exist between analyte concentrations, but are not discussed in this work.

***Calculations***

The concentration of As (in ppb) in solution was converted to mass concentration in the soils. Solution concentration was multiplied by the dilution factor and the digested solution weight (g) and divided by the dry weight of the solid soil sample (g) prior to digestions. An example calculation (e.g. sample WK1 0-5 cm) to obtain arsenic concentrations of the original solid can be seen below:

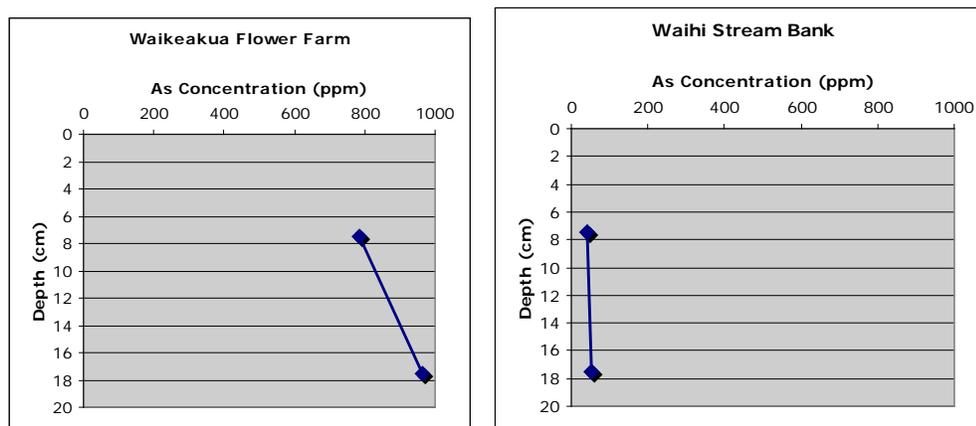
$$\frac{(50.7 \text{ ppb})(20)(92.9 \text{ g})}{(0.196 \text{ g})} = 480000 \text{ ppb}$$

Elemental concentrations of As in ppb in the original solid were divided by 1000 to report solid concentration of As in ppm.

## 4. RESULTS

### 4.1. Preliminary surface soils

The ICP-MS analysis of the surface soils gathered on 3 February 2009 took place on 19 February 2009 and revealed concentrations of arsenic 18 fold higher in the flower farm than near the stream bank (Figure 11). Arsenic concentrations were 785 and 42 ppm for the 0-15 cm subsample and 963 and 54 ppm for the 15-20 cm subsample for the flower farm and stream bank samples, respectively.



**Figure 11** Preliminary surface soil As concentrations

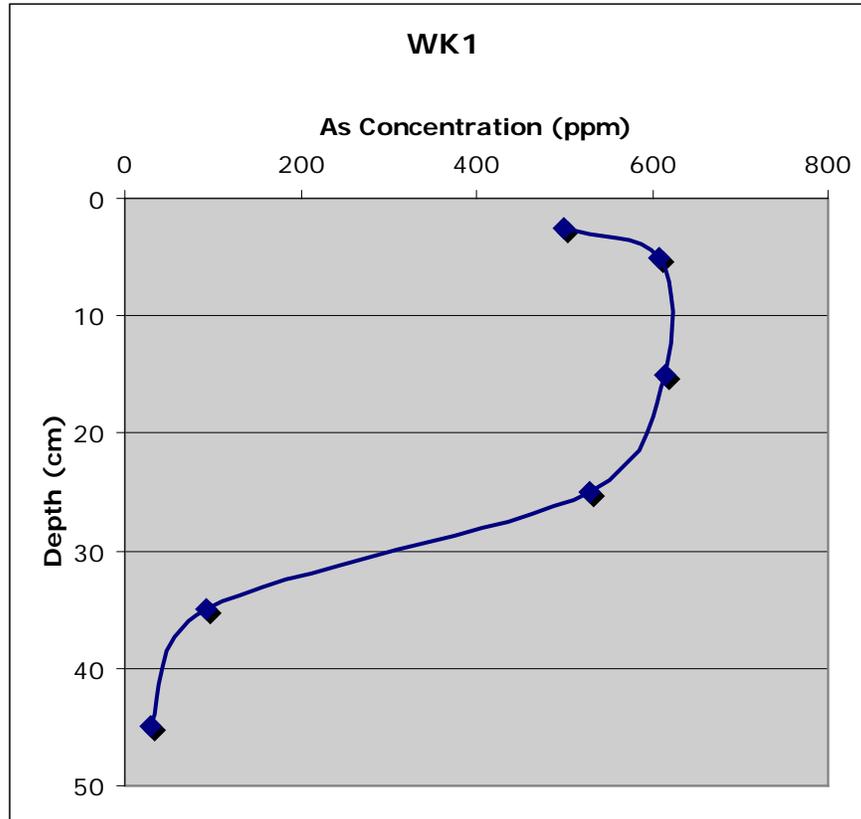
### 4.2. Soil cores

Arsenic concentrations (in ppm) for subsamples of all 6 cores can be found in Table 2. Please note the following; 1) the 0-10cm subsample was further divided into two subsamples for the WK1 core, 2) the WK2 core only reached a depth of 33cm, and 4) the depth increments for the WK3 core vary and exact depth ranges can be found in Appendix IV.

Depth (cm)	WK1	WK2	WK3	LA	WAI	KU
0-5	499	568	695	23.0	43.8	23.6
5-10	607		759			
10-15	615	913	805	22.9	44.1	23.1
15-20			490			
20-25	528	502	226	23.4	42.1	23.6
25-30			74.3			
30-35	93.4	489	61.8	20.8	22.8	24.9
35-40						
40-45	30.2				17.8	23.9
45-50						

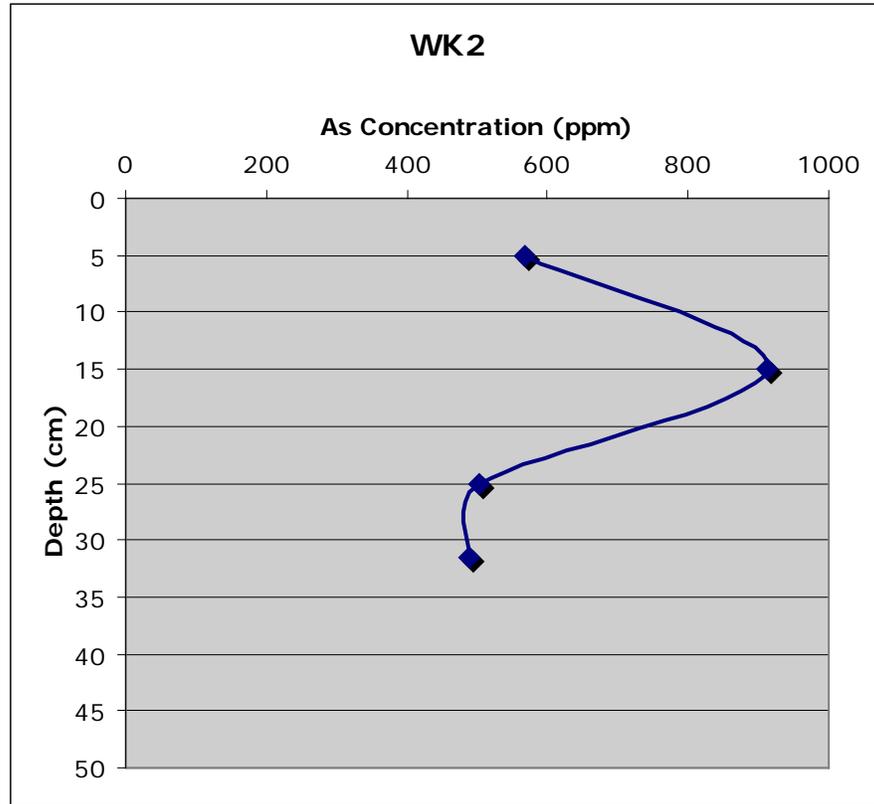
**Table 2** Arsenic concentrations for soils cores

The ICP-MS analysis for the WK1 core occurred on 23 April 2009. Arsenic concentrations for the WK1 soil core dramatically decrease below a depth of 30 cm (Figure 12). Subsamples from the surface to 30 cm have arsenic concentrations ranging from 499-615 ppm. The 30-40 cm and 40-50 cm subsamples contain quantities below 100 ppm As.



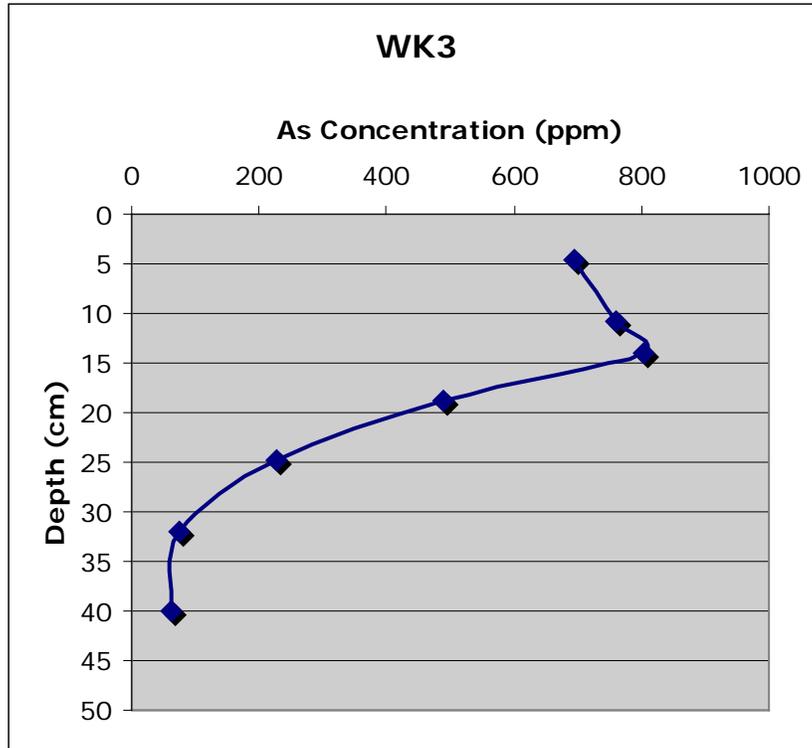
**Figure 12** Arsenic concentrations in the WK1 core taken from the Waikeakua gardenia farm

The ICP-MS analysis for soil cores WK2, LA, WAI, KU, and WK3 took place on 11 November 2009. The subsample with the highest concentration of As of all cores (913 ppm) was found in the 10-20 cm depth range of the WK2 core. Rocks prevented soil collection below 33 cm, but all subsamples from the WK2 location contained As levels above 480 ppm (Figure 13).



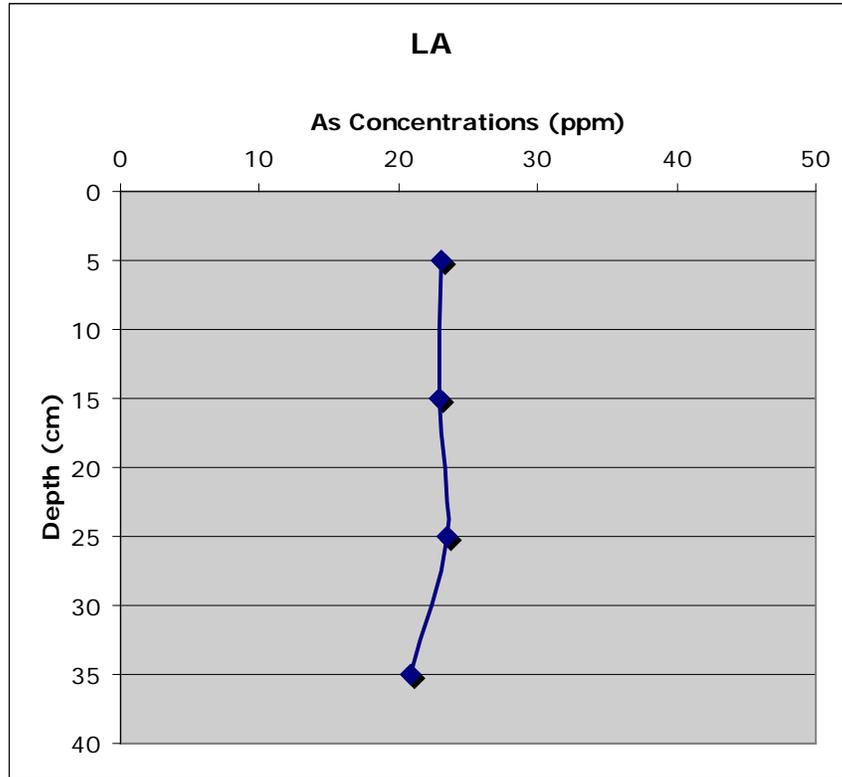
**Figure 13** Arsenic concentrations in the WK2 core obtained in forested area approximately 350 m above the Waikeakua gardenia farm

The WK3 core displays a variability of As similar to that observed in the WK1 core (Figure 14). These cores were collected in close proximity to each other in the same flower farm, hence the results indicate that the distribution of As and enrichment likely are similar throughout the farm.

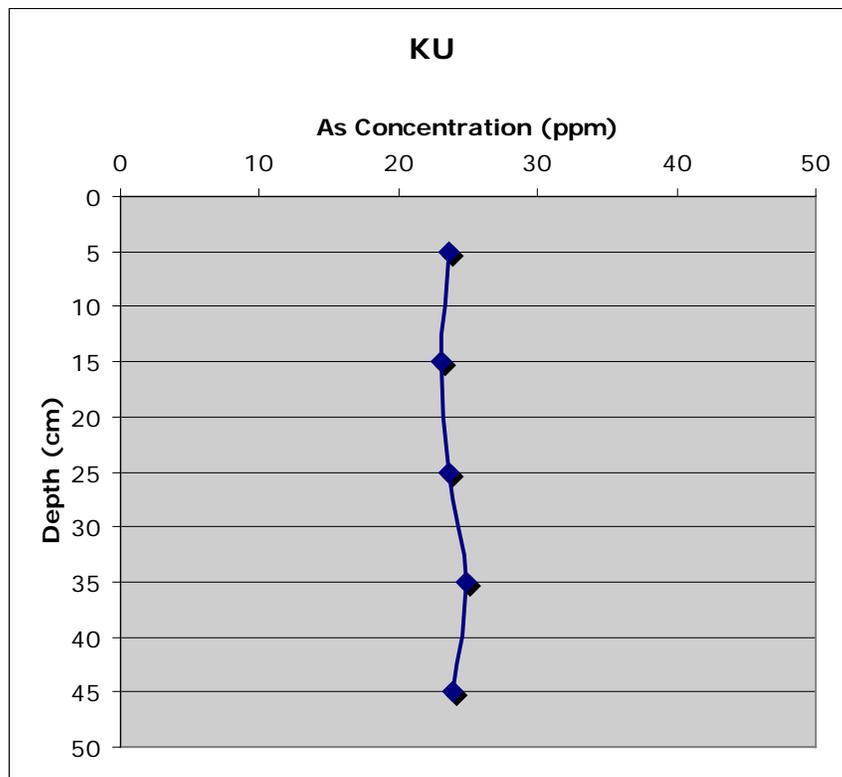


**Figure 14** Arsenic concentrations in the WK3 core taken from the Waiveakua gardenia farm

Arsenic concentrations in the LA and KU cores remained below 25 ppm for all subsamples (Figures 15 and 16, respectively). The maximum difference in As between subsamples on a given core was 2.63 ppm and 1.77 ppm for the LA and KU core, respectively, demonstrating the relatively uniform distributions of As with depth.

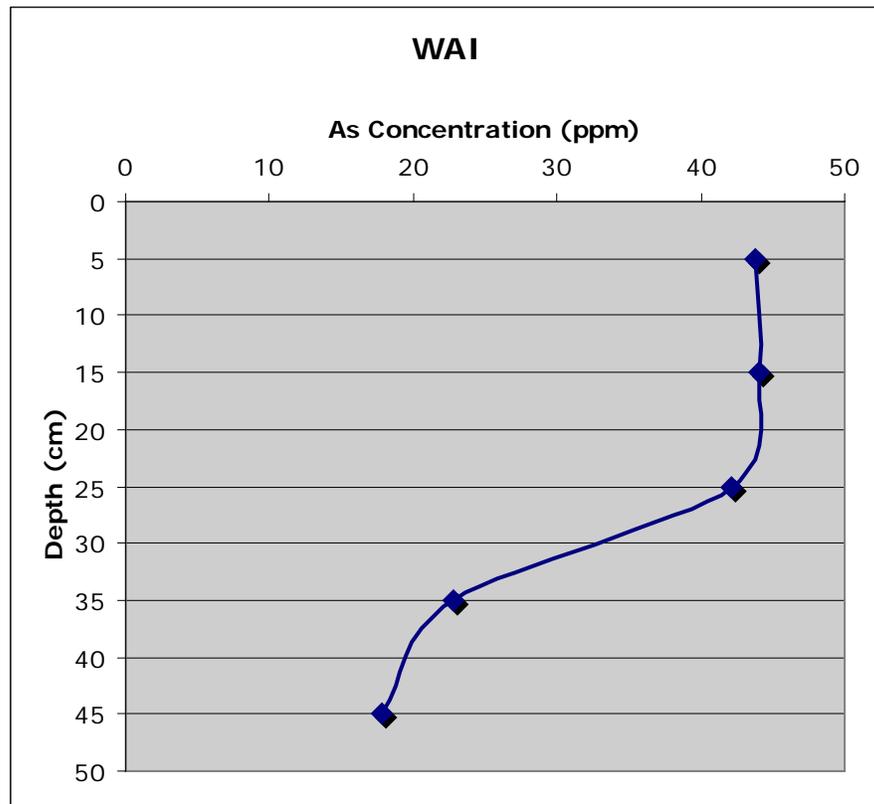


**Figure 15** Arsenic concentrations in the LA core taken from the Lyon Arboretum



**Figure 16** Arsenic concentrations in the KU core taken from a fallow pineapple field

The arsenic concentrations in the WAI core span between 43.8 ppm at the surface soil and 17.8 at a depth of 45 cm (Figure 17). The near surface sections of WAI contained nearly two fold concentrations of arsenic compared to the LA and KU cores, although concentrations were hundreds of ppm below those observed at any of the WK sites.



**Figure 17** Arsenic concentrations in the WAI core taken from a fallow sugarcane field

### ***Quality control of ICP-MS***

Digested splits of standard reference material (SRM) MESS1 and acid blanks were run through all procedures for quality control. All As values determined by the ICP-MS for MESS1 were within the coefficient of variation of the certified values. Concentrations of As in the blanks carried through the digestion procedure and ICP-MS

analysis contained an equivalent of 0.15-0.26 ppm As when calculated back to sediment dry weight. These values suggest no significant contamination occurred during sample preparation or analysis. Sediment concentrations of As in soil samples were therefore not blank corrected. Replicate (triplicate) analyses of solutions by ICP-MS yielded precisions on the order of 0.2 to 1.5% for standards and blanks, 0.2 to 2.6% for MESS1, and 0.1 to 1.4% Relative Standard Deviation (RSD) for soil samples. The variability in the As concentrations between separate subsamples of the same soil interval (i.e duplicate digestions) ranged from 0.2 to 12% RSD although the majority of duplicated displayed As concentrations within 1 to 3%.

#### **4.3. Fern Material**

Due to the time constraints on this project, analysis of plant material was not completed in time to be included in this report. The uptake of As by both species *Nephrolepis exaltata* and *Pteris vittata* will be determined by ICP-MS analysis of As in roots and shoots in the near future. These data may provide useful information for remediation of As contaminated soils in Hawaii as these ferns may have potential to sequester As in above ground biomass.

## 5. DISCUSSION

### 5.1. General overview of all cores

The results from this study show a wide range of arsenic concentrations between soil cores. The 40-45 cm interval from the Waipahu (WAI) sugarcane field core contained the lowest concentration of As with 17.8 ppm and the 10-20 cm surface soil interval from the Waikeakua 2 (WK2) core contained the highest concentration of As with 913 ppm. The three Waikeakua cores (WK1, WK2, WK3) displayed the highest overall enrichment of As, with a majority of the intervals having concentrations above 400 ppm. Surprisingly, the peak As concentration of 43.8 ppm in the WAI core was substantially lower than found in the WK cores. The Lyon Arboretum (LA) and Kunia (KU) cores only reached maximum As concentrations of 23.0 and 23.6 ppm, respectively. These are relatively low compared to the other cores but remain slightly above the documented background concentrations of 2-20 ppm of As in Hawaiian soils (DeCarlo et al., 2005; Cutler et al., 2006).

### 5.2. Spatial and vertical distributions of As

#### *Cores collected from Waikeakua gardenia farm and forested area along Waikeakua Stream*

##### *WK1 and WK3 from gardenia farm*

The WK1 and WK3 sites were chosen for coring based on the results of the preliminary sample collection data. The nearly 20 fold elevated As concentrations in both surface soil samples of the Waikeakua flower farm compared to the Waihi stream bank (collected on 3 February 2009) supported the hypotheses that anthropogenic (agricultural) activity elevates As concentrations in soils. The As concentration profile for the WK1 core, seen in Figure 11, displays a drastic decrease in the concentration of

As below 30 cm. The As concentrations in the WK1 core at the 5, 10, 20 and 30 cm depths are in the range of 500 ppm or more. Arsenic concentration peaks in the 10-20 cm interval. The hypothesized source of As, in either fertilizers or pesticides, would be applied directly to the surface, so the greatest As content might be expected there. However, peak As concentrations were found in subsurface intervals and may result from a combination of agricultural tilling and the strong binding properties of As to soil iron oxide and hydroxide groups. The presence of numerous green fertilizer pellets on surface soils during sample collection in February and March provides evidence of fertilizer application in this flower farm. An abundance of fertilizer pellets was also observed in the flower farm when the WK3 core was collected on 12 September 2009. The WK3 core As concentration profile (Figure 14) is similar to the WK1 core (Figure 12) and displays a subsurface maximum followed by a drastic decrease below about 30 cm depth.

Arsenic concentrations in the range of 500 ppm or more from the WK1 and WK3 cores likely resulted from the application of superphosphate fertilizers or ironite to the gardenia trees in the flower farm. The application of fertilizers high in phosphate would be beneficial to the Waikeakua flower farm because phosphate is essential for flowering. The hypothesis that As in this gardenia garden is derived from superphosphate fertilizers should be tested further by analyzing the As content of the pellets present in the grove. The determination of the As concentration in the pellets could potentially reveal the magnitude of the source of As to the soil in this study as well as in the SPM in the Waikeakua stream noted by DeCarlo et al. (2004). A number of these pellets were recovered when the WK3 core was collected on 12 September 2009, but due to time constraints were not analyzed prior to the writing of this thesis. Knowledge of the exact

As content of the fertilizers used in the gardenia farm could help improve our understanding of how well As is retained in Hawaiian soils. It is possible that the repeated application of fertilizers with relatively low concentrations of As (e.g., < 41 ppm As, noted in products of Agrium US Inc., Belle Plaine Coop., Black Diamond Organics, Crop Production Services Inc., and Earthsoils ) could have resulted in the high concentrations seen in the gardenia farm. Fertilizers need to be periodically applied because the P content is readily taken up by plants and needs to be replenished. The As introduced to the soil through these fertilizers, however, would not be taken up by the plants, especially if they are not hyperaccumulators, and would accumulate over time, elevating the concentration in the soil. If Ironite® fertilizers with between 3,000-6,2000 ppm As were applied to the gardenia farm, then the concentration of As observed in the soil could have accumulated with fewer applications (i.e., likely in a shorter period of time).

### ***WK2 from forested area mauka of gardenia farm***

The WK2 core sampling location was hypothesized to have As concentrations near the Hawaiian background levels because of the apparent lack of agricultural activity in the area. The WK2 core was collected in a forested area roughly 350 m above the location of WK1 and WK3 and 20 m in from the Waikeakua Falls trail. The relative position of the cores can be seen in Figure10. This site was hypothesized to be far enough away from anthropogenic activity that may contribute As to the soil. The vegetation at this collection site was overgrown and appeared natural, and showed no signs of any recent clearing for agriculture or any application of fertilizer. Rocks that

inhibited soil collection below a depth of 33 cm suggest that the area is not particularly suitable for agriculture. However, analysis of the WK2 core revealed As concentrations well above natural background levels of 2-20 ppm (DeCarlo et al., 2005; Cutler et al., 2006). The concentration of As in all intervals of the WK2 core were above 450 ppm and the highest concentration of As seen in any of the core subsamples (913 ppm) was found in the 10-20 cm interval of the core obtained from this site. If collection of soil was not inhibited by rocks at 33 cm it is hypothesized that the As concentration profile for WK2 would mimic those seen in WK1 and WK3, with As levels dropping below 100 ppm in the deepest intervals.

The elevated concentrations of As observed in the WK2 core are very likely due to previous anthropogenic activity in this area. The presence of an old bridge across the Waikeakua stream and an abandoned automobile near the WK2 collection site were noted on 10 March 2009 when the core was collected. Concrete housing foundations were also present and may represent the remnants of historic construction. It is possible that the use of CCA as a wood preservative in construction materials (Savory and Wills, 1984 as cited by Matschullat, 2000; US EPA) could have contributed to the observed As levels, but no decaying debris was observed to support this hypothesis. It is also possible that the WK2 location was historically in a region of agricultural activity. Over 100 years ago, Manoa Valley had been extensively cleared (deforested) for agriculture. High concentrations of As in the WK2 core may be derived from historical application of As containing pesticides used to clear roads of weeds in addition to protecting crops (W. Cutler, *pers. comm.* 2009). The Waikeakua Falls trails resembles a dirt/gravel road more than a hikers' trail. Arsenical pesticides may have been used as a way to maintain the

road for agricultural vehicular traffic. It wasn't until 1918 that the Lyon Arboretum was established by the Hawaiian Sugars Plantations Association (HSPA) to restore the Manoa Valley watershed and reforest the valley with various tree species. Prior to the establishment of the arboretum, it is possible that agricultural practices similar to those observed in the gardenia farm were applied in this area. The overgrown and forested appearance of the WK2 site today may reflect efforts put forth by the HSPA to restore Manoa Valley from the stresses associated with agriculture. Because As binds so strongly to the Fe rich lateritic soils, concentrations of As in soils from this location would remain elevated.

#### ***Fallow agricultural fields of Kunia and Waipahu***

Soil cores taken from the historical pineapple and sugarcane agricultural fields of Kunia and Waipahu, respectively, were hypothesized to display As concentration depth profiles similar to the WK1 profile. However, cores from Kunia and Waipahu showed relatively low concentrations of As in the soil column. Neither the KU nor the WAI core contained As concentrations above 50 ppm, although WAI concentrations were above typical Hawaiian background levels of 2-20 ppm (DeCarlo et al., 2005; Cutler et al., 2006). The range of As concentration in the KU core spanned between 23.1 and 24.9 ppm, displaying a nearly constant depth profile. Surface As concentrations in the WAI core were twice those found in the 30-50 cm depths, approximately 40 ppm and 20 ppm, respectively.

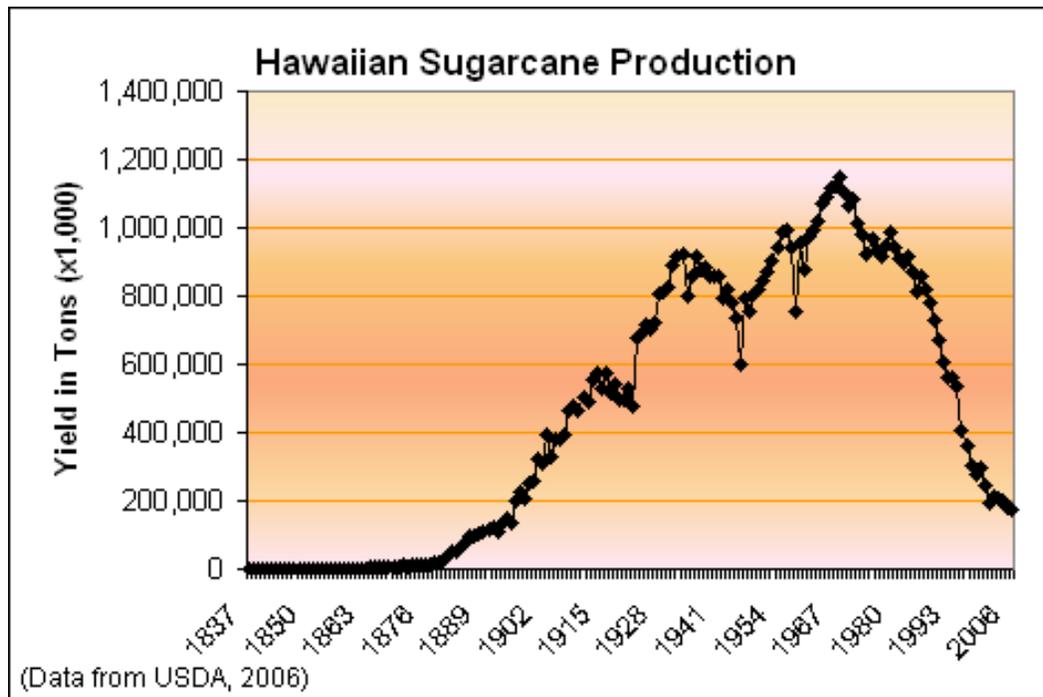
Relatively low concentrations of As were found in the KU and WAI cores compared to the WK cores. The Waieakua flower farm housed healthy gardenia trees and soil littered with fertilizer pellets. Neither the Kunia nor the Waipahu field showed

obvious signs of recent fertilizer application, although these areas were likely used extensively for agricultural activity for > 100 years of plantation agriculture.

Disseminated pineapple plants and broken, scattered sugarcane stalks present in KU and WAI, respectively, provide evidence of previous agricultural activity in these regions.

***Island of Hawai'i comparison to KU and WAI cores and decline of agriculture***

Elevated concentrations of As have been documented in former sugarcane fields on the island of Hawai'i (Cutler et al., 2006). The application of sodium arsenate (for weed control) on the Ola'a Plantation on the Big Island between the 1930's-1960's appears to be the source of As to these soils (Cutler et al., 2006). Because the production of sugarcane and other forms of agriculture were historically extensive in the state of Hawai'i (Figure 18) it is possible that As contamination of soils occurred across all islands.



**Figure 18** Hawaiian sugarcane production 1837-2006 (United States Department of Agriculture)

Surface soils (2-10 cm) obtained from Kea'au, Hawai'i revealed As concentrations of several hundreds of ppm (Cutler et al., 2006). Similar concentrations might be expected in the surface interval of the WAI core, since the core was also obtained from a sugarcane field that was still in production some twenty years ago. However, the relatively low concentrations of As seen in the WAI core may provide evidence that sodium arsenate was not applied to sugar fields on the island of O'ahu as was common on the island of Hawai'i. Superphosphate fertilizers may also be excluded as a source of As to this sugarcane field, since its application is believed to contribute to highly elevated As in soils. Nitrogen enriched fertilizers may have proven more beneficial in Waipahu, since sugarcane crops do not produce flowers and would not require superphosphate fertilizers.

The discontinued harvesting of pineapple at the Kunia site likely results from the decline in Hawaiian pineapple production and acreage across the entire state of Hawai'i throughout the 20<sup>th</sup> century. According to the National Agricultural Statistics Service, the state produced 212,000 tons of pineapple over 14,000 acres in 2005 (Hidano, 2005), significantly lower than the 700,000 tons across roughly 35,000 acres in 1987 (Martin, 1998). The 1987 acreage for pineapple agriculture is less than half what it was for the state in 1955 when 76,700 acres across the state were dedicated to pineapple production (Takeguchi et al., 2009).

Abundant debris of remnant plastic sheeting littered both the Kunia and Waipahu sites and debris was present in all intervals of both cores. Plastic sheeting has often been laid in rows of agricultural fields as a method to control annual weeds and avoid using pesticides (Deputy and DeFrank, 2001), which may contain As (Campos, 2002; Yokel

and Delistraty, 2003; Cutler et al., 2006). Crops were planted through the plastic sheeting but weeds could not readily grow upwards and puncture the plastic. This practice may have had beneficial effects in that it reduced potential As contamination that would derive from extensive use of pesticides. Nitrogen rich fertilizers may have been applied on the fields of KU and WAI instead of P-rich fertilizers. This would also decrease the quantities of As introduced to soils because As does not follow N in the environment as it does P. Finally, because the WAI core is from a field in the relatively dry leeward O'ahu, pesticides might not have been needed as much as in the high growth and wet windward Hawai'i fields.

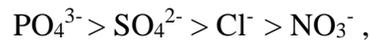
### ***Lyon Arboretum***

The results from the core collected from the Lyon Arboretum were similar to those found in the Kunia core. The concentration of As throughout the core was nearly constant. The levels of As in the LA core ranged from roughly 20-23.5 ppm. This is close to the maximum background levels of 20 ppm reported for Hawaiian soils (Cutler et al., 2006). Interestingly, one might have expected more As to be present at this site because many plants in the arboretum grounds were originally grown in greenhouses and were likely fertilized before being planted around the property. However, the LA core was obtained from a grassy slope and not in the immediate proximity of any plants.

### **5.3. Fundamental chemistry**

Tropical soils dominated by Fe or Al oxides and hydrous oxides have variable surface charges that depend on soil pH and on the adsorption of various species (Sposito, 1984). These phases exhibit a zero point of charge (ZPC) at higher pH than many other

soil components (Uehara and Gillman, 1981 and Sollins et al., 1988 as cited by Schlesinger, 1997) such as quartz and kaolinite found in continental settings. At the ZPC, the number of cation and anion exchange sites is equal (Schlesinger, 1997). Negative positive residual charges on the Fe and Al oxyhydroxides of Hawaiian latosols make them particularly suitable to bind anions. Greater anion adsorption capacity also occurs on poorly crystalline forms of Fe because they have a larger surface area than crystalline forms (Parfitt and Smart, 1978 and Johnson et al., 1986 as cited by Schlesinger, 1997). Anion adsorption occurs in the following sequence



where sulfate may be added to the soil from acid rain (Schlesinger, 1997). The low availability of phosphorus in tropical soils is attributed to the strong adsorption of phosphate. The strong binding of  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  to soils is known as specific adsorption and these anions are believed to replace  $-\text{OH}$  groups on the surface of minerals (Hingston et al., 1967 and Guadalix and Pardo, 1991 as cited by Schlesinger, 1997). The specific adsorption of  $\text{PO}_4^{3-}$  may therefore release  $\text{OH}^-$  or water to the soil (refer to Figure 6). The strong adsorption of  $\text{PO}_4^{3-}$  in tropical soils is thought to be applicable to its chemical analogue  $\text{AsO}_4^{3-}$  since As can substitute for P in the mechanism for adsorption onto iron oxides.

### **5.5. Peak As concentrations in subsurface interval of cores**

The subsurface maximum of As in the 10-20 cm interval for soil cores WK1, WK2, WK3, and WAI, may be attributed to a combination of natural and anthropogenic processes. Higher concentrations of As in subsurface soil intervals may simply result

from prior periods when rates of fertilizer application were greater, especially for the WAI core. Because Hawaiian sugarcane production has drastically decreased over the last few decades (Figure 17), maximum As concentrations in the WAI core may underlay soils deposited post agriculture. However, this assumption is highly unlikely because soil deposition would not occur so rapidly. Nor would this hypothesis hold true for the WK1 and WK3 cores which were obtained in a farm where agriculture continues today. The high concentrations of As seen in the surface soils gathered from the Ola'a plantation in Hawai'i by Cutler et al. (2006), however, is consistent with the specific adsorption of As to iron oxides, even under conditions of high precipitation.

In the case where fertilizers continue to be applied (WK1 and WK3) peak concentrations of As in subsurface intervals may result from some uptake of  $\text{AsO}_4^{3-}$  with  $\text{PO}_4^{3-}$  by the gardenia plants. For example, several different fern species have been found to extract As from soils (Ma et al., 2001; Tu and Ma, 2004; Srivastava et al., 2005; Srivastava et al., 2006) via the phosphate transport system (Wang et al., 2002). To support this hypothesis material from the gardenia plants in this farm would need to be analyzed for As to determine if plants enrich As. However, it would be unlikely for As concentrations to decrease in the surface soils when high quantities of P are available for plant uptake. Previous studies have shown that the accumulation of As in hyperaccumulator plants decreases with the increased availability of P in soils (Wang et al., 2002; Tu and Ma, 2004).

Maximum concentrations of As at the subsurface may also be linked to high concentrations of P at the surface. Campos (2002) and Peryea and Kammereck (1997) argue that elevated levels of  $\text{PO}_4^{3-}$  may increase the mobility and solubility of As in soils.

If so, then high levels of P present in fertilizers could mobilize As to subsurface soils below the root zone, where P may not be as abundant. Phosphorus levels should be expected to decrease with depth in agricultural fields because fertilizers are only applied to the surface. Below the zone of maximum P concentrations in the soil column, more surface sites on iron oxides will be available for specific adsorption of  $\text{AsO}_4^{3-}$  to the soils.

Because  $\text{AsO}_4^{3-}$  has a strong affinity for iron oxides, it may prove beneficial to also investigate how the iron content varies in soil cores. An increase in iron concentration in the 10-20 cm interval may possibly account for the increase in As concentrations. Phosphorus concentrations might also be expected to peak where the iron content is maximized, but P may be readily taken up by plants at the surface before it can mobilize downward. Low availability of P is characteristic of tropical soils because of the strong affinity of  $\text{PO}_4^{3-}$  to iron oxides (Hingston et al., 1976 and Guadalix and Pardo, 1991 as cited by Schlesinger, 1997). If fertilizers add  $\text{PO}_4^{3-}$  to surface soils with low P content, then As, which is not essential for plant growth, can substitute for P and bind with iron oxides (Figure 6) as the  $\text{PO}_4^{3-}$  is removed by the plants.

## 6. CONCLUSIONS

This study investigated the spatial distribution of As on the island of O'ahu with particular focus on the impact of agricultural land use. The vertical distribution of As in soil cores was also examined. Historical agricultural locations were hypothesized to display high As concentrations based on the surface of As concentrations found in the preliminary soil analysis of the WK location. Unexpectedly, both the KU and WAI cores had relatively low As concentrations, with concentrations in the KU core just over the maximum Hawaiian background levels and WAI about twice that, peaking at 43.8 ppm. The WK1 and WK3 cores, which were sampled in a flower farm that showed obvious recent fertilizer application, contained As concentrations in the range of 500 ppm or more. Interestingly, the interval containing the highest concentration of As in this study was found in the WK2 core which had been expected to exhibit near background concentrations of As.

The use of other methods of weed and pest control, such as plastic sheeting, may account for the unexpectedly low concentrations of As seen in the KU and WAI cores. The As concentrations in the WK1 and WK3 cores support the hypothesis that superphosphate or ironite fertilizers, which have been shown to be enriched in As (Charter et al., 1995), serve as a source of As to soils. The As concentrations in these cores are also consistent with the work of DeCarlo et al. (2004) and deGelleke (2007), who reported elevated concentrations of As in areas of agricultural activity.

Four of the six soil cores (WK1, WK2, WK3, and WAI) exhibited peak As concentrations in the 10-20 cm interval; in contrast, the LA and KU cores had nearly constant As profiles. The subsurface maxima may result from a variety of either natural

or anthropogenic processes, including specific adsorption, mobility enhanced by competitive adsorption, or agricultural tilling.

Time constraints prevented analysis of the fern material for both the *Pteris vittata* and *Nephrolepis exaltata* fern species in either the As contaminated or uncontaminated soils. The ability of these species to accumulate As in roots versus shoots from iron oxide soils will be evaluated in the near future and may provide useful information on the potential of phytoremediation of As contaminated sites in Hawai'i.

## APPENDIX II. Detailed Digestion Procedure

### MARS Xpress Microwave Digestion Procedure

Keep in mind:

1. Wear gloves when handling samples.
2. The spatula tip used to weigh out the samples should never touch the counter.
3. Check the vessel for pinhole leaks by holding it up to the light and looking for dark spots in the plastic.
4. MESS-1 weight is 0.100g.
5. Sample weights are around 0.100g.

Method:

---

#### Weighing the samples

1. Put the wax paper on the scale and zero the balance. Add sample slowly waiting for scale reading to stabilize until you have anywhere from 0.0900-0.1100g. Closer to 0.100g is desire.
  - a. It helps to fold the wax paper diagonally both ways for easy transfer to the vessel. Use wax paper if you can because the weighing trays are harder to get the sediment off of.
2. Record the initial sample weight.
3. Pour the sample into the clear plastic vessel. Be sure to get as little as possible on the vessel wall. Gently knock the vessel on the table to get all sediment to the bottom. Use DI water to help transferring the sediment into the vessels.
4. DO NOT DO THIS STEP IF you used DI water. Weight the wax paper to check if there is a significant amount of residue. If there is more than 0.0001g still on the paper subtract that weight from your initial weight value and record the true net weight.
5. Repeat steps 1-4 for each sample being digested.
6. Also, weight out 0.1000g of the standards (MESS-1) and Montana Soil following the same method and pour into respective recorded vessels.

The following steps have to be performed in the laminated fume hood (the air blowing towards you), keep the vessels on the side of you to avoid breathing acid fumes.

7. To add acid to the bomb you need to get a bottle of Trace Metal Grade Concentrated Nitric Acid (or Distilled Nitric Acid). Keep the bottle in the plastic bag and only remove the cap. Be sure to be very careful with this *strong* acid and keep it clean and in the bag.
  8. To open the vessels every time you add acid: hold the screwing cap and the white stopper in your hand to ensure no contamination of the caps.
  9. Pipette 4mL of Nitric Acid Trace Metal Grade into each vessel by rotating the vessel as you release the acid slowly from the pipette in order to wash any sample from the walls. Avoid touching the tip of the pipette to the side of the vessel!
  10. Add 2mL of Hydrochloric Acid Trace Metal Grade and 1mL of Hydrofluoric Acid to all vessels the same way.
  11. Hold the vessel nearly horizontal at eye level and gently rotate it to *make sure that all of the solids are in the solution* and not on the wall.
  12. Put the caps back on. Screw them on without forcing and then twist for 30 degrees more.
  13. Place the vessels in the rack. Note the position of which vessel.
- 

#### Digestion

14. Place the rack into the MARS Xpress Microwave. Make sure it is in its right spot: the base has a notch in which the rack goes to.
15. Turn the microwave and the laptop ON. Open the Synergy Prep program to control the microwave remotely. Make sure you are connected to the instrument. Open the method you like to use. For sediment digestion:
  - 1600W; 75%; 10min Ramp Time; 185 Temp; 0 PSI; 45 min Hold Time

16. After the digestion is done, remove the turntable from the microwave and place it under the hood.
  17. Take off the screwing caps and place them in the hood to reduce chance of contamination. Rinse the white stoppers with a little bit of DI water letting the excess fall back into the vessel. This can be done by rotating the top in the vertical position and squirting it with a bottle of DI water. After the top has been rinsed place in its respective cap.
- 

#### Evaporate the solvents from the sample

18. Transfer the vessels from the digestion rack (40 spots) to the evaporation rack (24 spots). Record the positions to keep track of your samples.
19. Place the XpressVap covers onto the vessels; they should sit onto the vessels nicely. Remember they go by twos, so you have to have an even number of vessels to evaporate (if odd number: take a vessel with just DI inside) and one of them should be the control cover with the hole for the temperature probe.
20. If you are not using all of the spots on the rack, you have to close Manifold arm ports that are unused with the Manifold arm plug.
21. Place the Manifold arm on the covers. Screw the Retaining Nut on the Manifold and Turntable. Use the Wrench to ensure proper locking of the Manifold arm.
22. Place the Turntable in the MARS Xpress microwave onto the notch.
23. Place the temperature probe into the glass tube through the control cover. Push the connector of the probe into its plug on the roof in the inside of the microwave.
24. Pass the suction line through the top of the microwave and connect it with the tube from the Manifold arm.
25. Select the Evaporation method that you desire to use. General drying:
  - 400W; 100%; 20 deltaT; 85 Temp; 0 Hold Time.

- OR: Power/Time control: 1600W; 55%; 5min Ramp; 0 psi; 0 temp; 90min Hold Time.
  - Turn the air pump ON in the adjacent hood.
26. MAKE SURE THE HOOD NEXT TO THE MICROWAVE IS CLOSED. THE DRYING PROCESS WILL GO FASTER.
  27. After each drying time, check the vessels to see if the solvents have evaporated. The vessels need to be pulled out as soon as all liquid has evaporated and preferably before the sample starts to bake and form chunks.
  28. Tare a ~125mL plastic bottle to be used for storing the sample. Label and record the tare weight in the lab notebook.
  29. Open a vessel under the hood. Take a clean graduated pipette (50mL at most). Measure out 10mL of 2% Nitric Acid and pour it down into the vessel by rotating the vessel in a nearly horizontal position to ensure there is no sample on the vessel walls (similar to Step 9). Pour solution into the tarred ~125mL plastic bottle. Remember to keep cleaner materials toward back and less clean materials in front of the hood.
  30. Rinse the vessel at least 2 more times this way.
  31. The final net bottle weight should be ~100g (greater than 90g but not exceeding 110g) for the bottle. Record final net weight in lab notebook.
  32. Repeat Steps 29-31 for each vessel and place the resulting sample bottles in a large Ziploc.
- 

Volumetric dilution to make 2% Nitric Acid:

1. Perform dilution in clean metal lab and use 8N Nitric Acid
2. Fill 1L plastic volumetric flask ~half full with DI water
3. Add 40mL 8N Nitric Acid using graduated cylinder
4. Fill rest of volume (to line) with DI water
5. Pour diluted acid into plastic bottle and wash graduated cylinder

## APPENDIX I. Preliminary surface soil and core spatial data

### Preliminary surface soils

Date	Sample Name	Latitude	Longitude	Depth (cm)	Comments
3 Feb 2009	#1	21.32846 N	157.7994 W	0-15	Raining conditions, soil muddy, reddish brown
3 Feb 2009	#2			15-20	
3 Feb 2009	#3	21.3283 N	157.8008 W	0-15	
3 Feb 2009	#4			15-20	Light rain, soil moist but not saturated, more blackish than reddish brown. Trash in area, glass near hole

### Core soil

Date	Core Name	Latitude	Longitude	Depth (cm)	Intervals	Comments
10 March 2009	WK1	21.32854 N	157.79936 W	50	6	0-10cm subsample broken into 0-5 and 6-10; in WK flower farm
10 March 2009	WK2	21.32969 N	157.79625 W	33	4	Deeper in Manoa Valley, hit rocks at 33
10 March 2009	LA	21.33384 N	157.80177 W	40	4	Lyon Arboretum
16 August 2009	WAI	21.37061 N	158.05423 W	45	5	Waipahu; old cane land; sugarcane stalks, plastic, silt screen debris
16 August 2009	KU	21.46806 N	158.05339 W	50	5	Minimal traffic pollution bc of trade winds Pineapples present, appears to have been pineapple farm
12 Sept 2009	WK3	21.32855 N	157.79933 W	40-44	7	need to measure post hole digger again for 2/3; green fertilizer pellets collected

**APPENDIX III. Fern data**

**Plant Data for *Nephrolepis exaltata* Species**

<b>Fern ID</b>	<b>Date Collected</b>	<b>Date Planted</b>	<b>Date Uprooted</b>	<b>Soil Type</b>	<b>Comments</b>
Control 1	12 September 2009	N/A	12 September 2009	N/A	yellow label, different vender than others according to Home Depot
Control 2	11 September 2009	N/A	12 September 2009	N/A	
1	11 September 2009	12 September 2009	15 November 2009	Clean	
2	11 September 2009	12 September 2009	17 November 2009	Clean	
3	11 September 2009	12 September 2009	17 November 2009	Clean	
4	12 September 2009	12 September 2009		Clean	yellow label, different vender than others according to Home Depot
5	11 September 2009	12 September 2009	19 November 2009	Contaminated	
6	11 September 2009	12 September 2009	19 November 2009	Contaminated	
7	11 September 2009	12 September 2009	19 November 2009	Contaminated	
8	12 September 2009	12 September 2009		Contaminated	yellow label, different vender than others according to Home Depot

**Plant Data for *Pteris vittata* Species**

<b>Fern ID</b>	<b>Date Collected</b>	<b>Date Planted</b>	<b>Date Uprooted</b>	<b>Soil Type</b>	<b>Comments</b>
Control 1	17 September 2009	N/A			
Control 2	26 October 2009	N/A			
Old	17 September 2009	17 September 2009	15 November 2009	Clean	Pre-existing shoots from original plant
New	17 September 2009	17 September 2009	15 November 2009	Clean	No shoots from original plant, but 2 newly sprouted shoots
3	17 September 2009	17 September 2009	15 November 2009	Contaminated	No shoots from original plant, but 1 newly sprouted shoots
4	17 September 2009	17 September 2009	N/A	Contaminated	Fern died

**APPENDIX IV. ICP-MS Data**

**ICP-MS Data 19 February 2009 preliminary surface soils**

Sub Sample	Mean Analyte Dilution Concentration of 75As (ppb)	Dilution Factor	Tare (g)	Soln+ Bottle (g)	Net Wt Soln (g)	Weight (mg)	Weight (g)	As Concentration (ppm)	As Concentration w/av. Duplicates (ppm)
Mean of 020309-1a	53.3	10	26.3796	126.1198	99.7402	100.4	0.1004	530	520
Mean of 020309-1b	56.5	10	26.3379	124.9043	98.5664	109.3	0.1093	510	
Mean of 020309-2a	66.8	10	26.2771	126.981	100.7039	104.3	0.1043	645	641
Mean of 020309-2b	71.4	10	26.3851	123.5122	97.1271	109	0.109	637	
Mean of 020309-3a	2.9	10	26.2505	125.2911	99.0406	102	0.102	28.2	28.4
Mean of 020309-3b	2.92	10	26.2756	126.1619	99.8863	102.1	0.1021	28.6	
Mean of 020309-4a	3.65	10	26.3735	126.3426	99.9691	100.6	0.1006	36.2	35.7
Mean of 020309-4b	3.56	10	26.3589	125.2878	98.9289	100	0.1	35.2	

ICP-MS Data 23 April 2009 WK1 core

Sub Sample	Mean Analyte Dilution Concentration of 75As (ppb)	Dilution Factor	Tare (g)	Soln+ Bottle (g)	Net Wt Soln (g)	Weight (mg)	Weight (g)	As Concentration (ppm)	As Concentration w/av. Duplicates (ppm)
WK1 0-5	50.7	20	25.1453	118.0090	92.8637	195.9	0.1959	481	499
WK1 0-5Dup	49.6	20	25.2077	125.4887	100.2810	192.3	0.1923	517	
WK1 6-10	57.9	20	25.1585	124.0267	98.8682	199.9	0.1999	573	607
WK1 6 10Dup	59.9	20	25.2788	126.4796	101.2008	189.0	0.1890	641	
WK1 10-20	60.6	20	25.2841	128.1598	102.8757	202.9	0.2029	614	615
WK1 10-20Dup	60.6	20	25.2193	123.6864	98.4671	193.4	0.1934	617	
WK1 20-30	50.3	20	25.3267	126.9761	101.6494	193.5	0.1935	528	528
WK1 30-40	9.09	20	25.1751	125.8278	100.6527	202.1	0.2021	90.5	93.4
WK1 30-40Dup	8.73	20	25.2992	129.3380	104.0388	188.9	0.1889	96.2	
WK1 40-50	3.20	20	25.2378	117.4873	92.2495	195.7	0.1957	30.2	30.2

ICP-MS Data 11 November 2009 LA, WK2, WAI, KU, WK3 cores

Sub Sample	Mean Analyte Dilution Concentration of 75As (ppb)	Dilution Factor	Tare (g)	Soln+ Bottle (g)	Net Wt Soln (g)	Weight (mg)	Weight (g)	As Concentration (ppm)	As Concentration w/av. Duplicates (ppm)
LA1 0-10	2.06	10	27.044	128.936	101.892	100.1	0.1001	21.0	23.0
LA1 0-10Dup	2.61	10	26.965	123.536	96.571	100.4	0.1004	25.1	
LA1 10-20	2.32	10	27.01	125.965	98.955	100.2	0.1002	22.9	23.0
LA1 20-30A	2.22	10	27.117	132.319	105.202	99.6	0.0996	23.4	23.4
LA1 20-30B	1.95	10	27.063	133.358	106.295	99.7	0.0997	20.8	20.8
WK2 0-10	55.7	10	26.995	127.781	100.786	98.8	0.0988	568	568
WK2 10-20	85.5	10	26.939	128.887	101.948	98.1	0.0981	889	913
WK2 10-20Dup	96.0	10	27.123	124.037	96.914	99.2	0.0992	937	
WK2 20-30	50.2	10	26.81	126.856	100.046	100	0.1	502	502
WK2 30-33	49.5	10	27.063	126.618	99.555	100.7	0.1007	489	489
WAI 0-10	4.52	10	26.929	123.552	96.623	99.7	0.0997	43.8	43.8
WAI 10-20	4.35	10	27.289	130.069	102.78	101.3	0.1013	44.1	44.1
WAI 20-30	4.22	10	27.032	126.524	99.492	99.6	0.0996	42.1	42.1
WAI 30-40	2.36	10	27.178	123.899	96.721	100.3	0.1003	22.8	22.8
WAI 30-40Dup	2.28	10	27.165	126.748	99.583	99.5	0.0995	22.8	
WAI 40-45	1.77	10	26.945	127.95	101.005	100.4	0.1004	17.8	17.8

Sub Sample	Mean Analyte Dilution Concentration of 75As (ppb)	Dilution Factor	Tare (g)	Soln+ Bottle (g)	Net Wt Soln (g)	Weight (mg)	Weight (g)	As Concentration (ppm)	As Concentration w/av. Duplicates (ppm)
KU 0-10	2.42	10	26.999	124.756	97.757	100	0.1	23.6	23.6
KU 10-20	2.28	10	26.986	128.378	101.392	100.2	0.1002	23.1	23.1
KU 20-30	2.32	10	27.123	126.248	99.125	99.8	0.0998	23.0	23.6
KU 20-30Dup	2.30	10	27.053	131.387	104.334	99.2	0.0992	24.2	
KU 30-40	2.57	10	27.304	124.848	97.544	100.8	0.1008	24.9	24.8
KU 40-50	2.35	10	27.233	128.389	101.156	99.5	0.0995	23.9	23.9
WK3 0-9	35.1	20	27.031	126.491	99.46	100.5	0.1005	695	694
WK3 10-12	35.9	20	27.235	133.572	106.337	100.6	0.1006	759	759
WK3 13-16	38.7	20	27.293	130.972	103.679	99.6	0.0996	805	805
WK3 17-21.5	23.6	20	27.06	130.569	103.509	100.4	0.1004	487	490
WK3 17-21.5Dup	23.7	20	27.001	131.487	104.486	100.1	0.1001	494	
WK3 22-28	11.0	20	27.266	129.176	101.91	99.2	0.0992	226	226
WK3 29-36	3.72	20	27.235	126.934	99.699	99.8	0.0998	74.3	74.3
WK3 36-44	3.06	20	27.169	128.428	101.259	100.2	0.1002	61.8	61.8

## REFERENCES

- Berg, M., H.C. Tran, T.C. Nguyen, H.V. Pham, R. Schertenleib, and W. Giger. (2001) Arsenic contamination of groundwater and drinking water in Vietnam: a human health threat. *Environmental Science* 35(13): 2621-2626.
- Campos, V. (2002) Arsenic in groundwater affected by phosphate fertilizers at São, Brazil. *Environmental Geology* 42:83-87.
- Charter, R.A., M.A. Tabatabai, and J.W. Schafer. (1995). Arsenic molybdenum, selenium, and tungsten contents of fertilizers and phosphate rocks. *Communications in Soil Science and Plant Analysis* 26(17-18): 3051-3062.
- Cullen, R.W. and K.J. Reimer. Arsenic Speciation in the Environment. *Chem. Rev.* (1989) 89:713-764.
- Cutler, W., N. Hue, M.E. Ortiz-Escobar, and T. Martin. (2006). Approaches to reduce bioaccessible As in Hawaii soils. *Proceeding of Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*. Monterey, CA.
- DeCarlo, E.H. and D.M. Thomas. (1985). Removal of arsenic from geothermal fluids by adsorptive bubble flotation with colloidal ferric hydroxide. *Environmental Science and Technology* 19(6): 538-544.
- DeCarlo, E.H., Beltran, V.L., and Tomlinson, M.S. (2004) Composition of water and suspended sediment in streams of urbanized subtropical watersheds in Hawaii. *Applied Geochemistry* 19: 1011-1037.
- DeCarlo, E.H., M.S. Tomlinson, S.S. Anthony. (2005). Trace elements in streambed sediments of small subtropical streams on O'ahu, Hawai'i: Results from the USGS NAWQA program. *Applied Geochemistry* 20:2157-2188.
- DeCarlo, E.H. and P.A. O'Day. (2008) Impact of arsenic speciation on mobility and bioaccessibility in tropical environments. Unpublished Data.
- deGelleke, L. Abundance and distribution of arsenic in Hawaiian soils and sediments. Unpublished Undergraduate Thesis, GES program, University of Hawaii, Honolulu, HI, 2007.
- Environmental Protection Agency (EPA). (2002) <http://www.aapfco.org/EPAZinc07-15.htm>
- Giambelluca, T.W., L.S. Lau, Y.S. Fok, and T.A. Schroeder. (1984). Rainfall frequency study for O'ahu: State of Hawai'i. *Department of Land and Natural Resources, Division of Water and Land Development*, Report R-73.

- Deputy, J. and J. DeFrank. (2001). Weed control options in landscape beds and groundcovers. *Landscape* L-12
- Hidano, R.W. Hawaii Pineapples Annual Summary 2005. National Agricultural Statistics Service in cooperation with Department of Agriculture, State of Hawaii Agricultural Development Division. 7 February 2006.
- Ma, L.Q., K.M. Komar, C.Tu, W. Zhange, Y. Cai, and E.D. Kennelley. A fern that hyperaccumulates arsenic. *Nature* (2001) 409:579.
- MacDonald, GA; Abbott, AT; Peterson, FL. 1983. Volcanoes in the Sea, 2<sup>nd</sup> Ed.: University of Hawai'i Press, Honolulu, HI.
- Martin, D.A. Hawaii Pineapples Annual Summary 1997. National Agricultural Statistics Service in cooperation with Department of Agriculture, State of Hawaii Agricultural Development Division. 9 April 1998.
- Matschullat, J. Arsenic in the geosphere-a review. *Science of the Total Environment* (2000) 249:297-312.
- Meador J.P., D.W. Ernest, and A. Kagley. (2004) Biaccumulation of arsenic in marine fish and invertebrates from Alaska and California. *Arch. Environ. Contam. Toxicol.* 47:223-233.
- Nordstrom, D.K. Worldwide Occurrences of Arsenic in Ground Water. *Science* (2002) 296:2143-2145.
- Nriagu, J.O. Arsenic Poisoning through the ages, Chpt. 1 of Environmental Chemistry of Arsenic by William T. Frankenberger 2002. *Marcel Dekker, Inc.*  
[http://books.google.com/books?hl=en&lr=&id=wryblpnw4DAC&oi=fnd&pg=PA1&dq=arsenic+poisoning+in+history&ots=OhFhdqAsuz&sig=hk2VbbVdnXmTbTXKw6wawtwIk\\_bc#v=onepage&q=arsenic%20poisoning%20in%20history&f=false](http://books.google.com/books?hl=en&lr=&id=wryblpnw4DAC&oi=fnd&pg=PA1&dq=arsenic+poisoning+in+history&ots=OhFhdqAsuz&sig=hk2VbbVdnXmTbTXKw6wawtwIk_bc#v=onepage&q=arsenic%20poisoning%20in%20history&f=false)
- Peryea, F.J. and Kammereck, R. (1997) Phosphate-enhanced movement of arsenic out of lead arsenate-contaminated topsoil and though uncontaminated subsoil. *Water, Air, and Soil Pollution* 93: 243-254.
- Schlesinger, William, H. Biogeochemistry, Second Edition. New York: Academic Press, 1997.
- Shiomi, K., Y. Sugiyama, K. Shimakura, and Y Nagashima. (1995). Arsenobetaine as the major arsenic compound in the muscle of two species of freshwater fish. *Applied Organometallic Chemistry* 9:105-109.
- Smith, E., P.A. Lopipero, M.N. Bates, and C.M. Steinmaus. Public Health. Arsenic epidemiology and drinking water standards. *Science* (2002) 296:2145-2146.

Sposito, Garrison. The Surface Chemistry of Soils. New York: Oxford University Press, 1984.

Srivastava, M., L.Q. Ma, N. Singh, and S. Singh. Antioxidant response of hyper-accumulator and sensitive fern species to arsenic. *Journal of Experimental Botany* (2005) 56(415):1335-1342.

Srivastava, M., L.Q. Ma, and J.A. Gonzaga Santos. (2006) Three new arsenic hyperaccumulating ferns. *Science of the Total Environment* 364:24-31.

Takeguchi, A., J. Hollyer, W. Koga, M. Hakoda, K. Rohrbach, H.C. S. Bittenbender, B. Buckley, J.B. Friday, R. Bowen, R. Manshardt, J. Leary, G. Teves, E. Herring, H. Zaleski, K. Leonhardt, and B. Eger. History of Agriculture in Hawaii. State of Hawaii Department of Agriculture. 29 November 2009  
<http://hawaii.gov/hdoa/ag-resources/history>

Tamaki, S; Frakenberger Jr., WT. 1992. Environmental biochemistry of arsenic. *Rev. Environmental Contam. Toxicol.* 124: 79-110

Thomas, R. (2001a). A beginner's guide to ICP-MS part 1. *Spectroscopy* 16(4): 38-42.

Thomas, R. (2001b). A beginner's guide to ICP-MS part 2. *Spectroscopy* 16(5): 56-60.

Tu, S. and Ma, L.Q. (2004) Comparison of arsenic and phosphate uptake and distribution in arsenic hyperaccumulating and nonhyperaccumulating fern. *Journal of Plant Nutrition.* 27 (7): 1227-1242.

United States Environmental Protection Agency Fact Sheet

[http://www.epa.gov/ogwdw/arsenic/regulations\\_factsheet.html](http://www.epa.gov/ogwdw/arsenic/regulations_factsheet.html)

United States Environmental Protection Agency. (2000). Introduction to Phytoremediation. National Risk Management Research Laboratory; Office of Research and Development. Cincinnati, Ohio.

Uttam, K.C, B.K. Biswas, T.R. Chowdhury, G. Samanta, B.K. Mandal, G.C. Basu, C.R. Chanda, D. Lodh, K.C. Saha, S.K. Mukherjee, S. Roy, S. Kabir, Q. Quamruzzaman, and D. Chakraborti. (2000) Groundwater arsenic contamination in Bangladesh and West Bengal, India. *Environmental Health Perspectives* 108(5): 393-397.

Vaughan, D.J. Arsenic. *Elements* (2006) 2:71-75.

Wang, J., F.J. Zhao, A.A. Meharg, A. Raab, J. Feldmann, and S.P. McGrath. Mechanisms of Arsenic Hyperaccumulation in *Pteris vittata*. Uptake Kinetics, Interaction with Phosphate, and Arsenic Speciation. *Plant Physiology* (2002) 130:1552-1561.

Wen, X.Y., De Carlo, E.H., and Li, Y.H. (1997). Interelement relationships in ferromanganese crusts from the central Pacific Ocean: their implications for crust genesis. *Marine Geology* 136:277-297.

Wrobel, K., K. Wrobel, B Parker, S.S. Kannamkumarath, and J.A. Caruso. (2002). Determination of As(III), As(V), monomethylarsonic acid, dimethylarsinic acid and arsenobetaine by HPLC-ICP-MS: analysis of reference materials, fish tissues and urine. *Talanta* 58:899-907.

Yokel, J. and Delistraty, D.A. (2003) Arsenic, lead, and other trace elements in soils contaminated with pesticide residues at the Hanford site. *Environmental Toxicology* 18: 104-114.

Zhao, F.J., S.J. Dunham, and S.P. McGrath. Arsenic hyperaccumulation by different fern species. *New Phytologist* (2002) 156:27-31.