

## Distribution and Abundance of Arsenic in the Soils and Sediments of O‘ahu, Hawai‘i

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**Abstract** Lack of high-spatial-resolution soil and sediment arsenic data for Hawai‘i has generated substantial disagreement between researchers and regulators regarding the magnitude of natural levels of arsenic in Hawai‘i and rendered difficult the defining of areas of anthropogenically elevated arsenic. Our earlier research into the occurrence of arsenic in terrestrial and marine environments revealed widely disparate concentrations of arsenic with no apparent spatial pattern. To better understand the distribution and abundance of arsenic in soils and sediments of O‘ahu, we collected an additional 64 samples at locations chosen to represent different environments with varying degrees of human impact. We found surface arsenic values that ranged from 0.28 to 740 ppm with a median concentration of 8.1 ppm, which is above the global median of 5 ppm and US soil median of 5.2 ppm. Higher concentrations of arsenic (up to 913 ppm) were encountered at depth in soil cores. The median arsenic in streambed sediments from one of our earlier studies of 6.1 ppm was comparable to the conterminous US median of 6.3 ppm; however, we encountered arsenic concentrations as high as 43.9 ppm (median = 8.60 ppm,  $n = 75$ ) in marine sediments in recent work off the leeward coast of O‘ahu. Overall, arsenic in the soils and sediments of O‘ahu is elevated relative to world and national values, but there still is no readily discernible pattern in the distribution of arsenic to explain these elevated values.

**Keywords** Arsenic (As) · O‘ahu · Hawai‘i · Soils · Sediments

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## 1 Introduction

### 1.1 Arsenic and Its Occurrence

Concern about the environmental and human health issues associated with arsenic (As) has existed for decades. Within the last few years, however, this concern has moved to the forefront as more of the world's population relies on groundwater as a source of *clean* drinking water (NRC 2001; Vaughan 2006; Reimann et al. 2009). Although As is a naturally occurring element in the Earth's crust and is commonly found as a trace constituent of rocks, soils, sediments, water, and biota (e.g., Li 2000; Kabata-Pendias 2001; Vaughan 2006), both natural and anthropogenic processes can elevate concentrations in ore bodies, groundwater, selected natural surface water bodies, soils, and sediments to toxic levels.

Paradoxically, As is classified as both an important micronutrient to some animals, including humans, and highly toxic to those same animals, as well as plants, at higher concentrations (ATSDR 2007). Chronic exposure to As has been shown to cause a variety of cancers (Wu et al. 1989; Smith et al. 1992) and is also associated with a variety of other human ailments (Cullen and Reimer 1989; NRC 2001; Jain and Ali 2000). The Bengal Basin of Bangladesh and West Bengal provides one of the most dramatic examples of how As impacts humans, where natural geologic conditions combined with intense human demand on groundwater resources have led to contamination of wells with As [1–1,000 µg/L or parts per billion (ppb)] (e.g., Nickson et al. 1998; van Geen et al. 2008). The situation in Bangladesh remains one of the greatest public health disasters in the world (Smith et al. 2000; Ahmed et al. 2004). Other areas in Southeast Asia also suffer similar problems. The current World Health Organization (WHO) and USEPA limit for As in drinking water is 10 µg/L (~10 ppb), and many wells in Bangladesh exhibit concentrations that vastly exceed this or the previously less stringent 50 µg/L criterion. Although the As source in Southeast Asia is thought to be largely of natural origin, As accumulations from recent and historical anthropogenic activities have revealed widespread impacts on soils, sediments, and groundwater throughout the world (Bhumbla and Keefer 1994; Huang 1994; Smith et al. 1998; Belluck et al. 2003).

Arsenic is the 47th most abundant of the 88 naturally occurring elements (Plant et al. 2005). It is ubiquitous in the lithosphere, albeit at relatively low concentrations ranging from 0.5 to 2.5 ppm (Kabata-Pendias 2001). It is the 48th most abundant element in the Earth's continental crust, with an average concentration of 1.7 ppm (Wedepohl 1995). Natural concentrations of As are highly variable. Weathering of As-containing rocks is considered to be the dominant natural source of As to the environment (Tamaki and Frankenberger 1992). Volcanic eruptions and hydrothermal activity are two other important natural sources of As (Matschullat 2000). Arsenic forms a broad range of organic and inorganic compounds and strongly complexes to solid metal oxides when present as an oxyanion (Fuller et al. 1993). The most important As-containing minerals are metal sulfides, including arsenopyrite, orpiment, and realgar (O'Day 2006). The weathering and oxidation of base metal sulfides in mineral deposits lead to the formation of many secondary As minerals that often coat the primary sulfides. These are typically arsenates or mixed arsenate-hydroxides of metals, such as calcium, cobalt, iron, magnesium, and nickel. The simple iron arsenate, scorodite ( $\text{FeAsO}_4 \cdot \text{H}_2\text{O}$ ), is, by far, the most common secondary arsenic mineral (O'Day 2006; Drahota and Filippi 2009). Mining of sulfide ores provides important metal resources in many areas, but mining activities can concentrate As and often subsequently release it to the environment in large quantities (e.g., Matschullat 1996; Matschullat et al. 2000).

Anthropogenic sources of As exceed the natural sources in the environment by 3:1 according to Mandal and Suzuki (2002), and according to Matchullat (2000), “[s]ixty percent of the anthropogenic As emissions can be accounted for by only two sources: Cu-smelting and coal combustion.” According to Pacyna (1987), As naturally occurs in coal and crude oil at the levels of 0.34–130 ppm and 0.0024–1.63 ppm, respectively, which accounts for its presence in flue gas, fly ash, and bottom ash from power plants.

In the USA and worldwide, industrial activities (smelting, S and P mineral processing, cement production, fossil fuel combustion, and geothermal power plants), waste incineration, fertilizer application, and the widespread use of arsenical pesticides during the twentieth century left residual As in surface and near-surface soils at concentrations ranging from 10 to 1,000s ppm (Matschullat 2000; Kabata-Pendias 2001). Soil As accumulations from agricultural pesticide applications have been reported at sites across the USA (Belluck et al. 2003; Robinson and Ayuso 2004; Yang and Donahoe 2007; Robinson et al. 2007). Senesi et al. (1999) reported the arsenic content in mineral and synthetic fertilizers ranged from 2.2 to 322 ppm with triple superphosphate having the highest level.

Liberal application of arsenical pesticides in tropical and semitropical areas has left a legacy of As accumulation and potential human and ecological risk. Evidence suggests that mineral weathering in tropical settings enhances As retention in soils, depending on the nature of the mineral alteration, rates of weathering, rainfall and runoff, and other environmental factors that influence As speciation (Cutler et al. 2006; Hue 2010; Hue and Ahmad 2012; Cutler et al. 2013; Hue 2013). Many sites of former agricultural or large-scale plantation production are now converting to urban or industrial uses, or lie fallow, with little knowledge of the potential hazard to humans or organisms posed by residual As in soils. Furthermore, as soils erode in high-rainfall regions, such as Hawai‘i, they may represent an important potential source of contamination of As to coastal marine environments (e.g., De Carlo and Anthony 2002; De Carlo et al. 2004, 2005; UHM [University of Hawai‘i at Mānoa] 2013), with currently unknown human and ecological implications.

Use of As has decreased as the awareness of the detrimental effects of even low concentrations of As in the environment has grown. For example, the last agricultural registration of inorganic As pesticide in the USA was canceled in 1993, although organic arsenicals still remain in some pesticides (Abernathy et al. 2003). Most recently, US wood treatment and manufacturing industries voluntarily agreed to stop using CCA as a wood preservative by the end of 2003.

Interestingly, the use of micronutrient fertilizers such as Ironite<sup>®</sup>, which are rich in trace elements including As (mean concentration 4,440 ppm), persists. Ironite<sup>®</sup> consists of essentially mine tailings from Iron King Mine in Humboldt, Arizona, to which other plant nutrients are added. The Arizona Department of Health Services (AZDHS 1998) concluded that “prolonged use of Ironite<sup>®</sup> in a residential setting does not appear to represent a health risk to residents of homes”; however, they also stated that their “...report does not consider exposures that may occur as a result of the potential uptake of contaminants into terrestrial garden plants and trees.” The AZDHS “...analysis considers exposures via ingestion, inhalation, and dermal contact”; it does not consider other pathways into the environment. Ironite<sup>®</sup> will be discussed in greater detail later in this article.

## 1.2 Geochemistry of Arsenic in Soils and Sediments

Arsenic exists in multiple oxidation states at earth surface conditions. Arsenite ( $\text{AsO}_3^{3-}$ ) and arsenate ( $\text{AsO}_4^{3-}$ ) are by far the most common As species found in the environment (Stoeppeler 1992). Pentavalent As shows many similarities in chemical behavior with

phosphorus due to the formation of the isostructural oxyanions phosphate ( $\text{PO}_4^{3-}$ ) and arsenate ( $\text{AsO}_4^{3-}$ ) (Goldschmidt 1958). Both  $\text{AsO}_4^{3-}$  and  $\text{PO}_4^{3-}$  have strong pH-dependent affinities for surface groups on hydrous iron (Fe) oxide and iron oxy-hydroxide minerals. A competitive chemical behavior of  $\text{AsO}_4^{3-}$  and  $\text{PO}_4^{3-}$  occurs in natural systems in the absence of oxidation-reduction reactions. This stems from the very similar second and third acid dissociation constants ( $\text{pK}_{\text{a}2}$  and  $\text{pK}_{\text{a}3}$ ) of their corresponding acids ( $\text{H}_3\text{AsO}_4$  and  $\text{H}_3\text{PO}_4$ ), which are near 7 and 12, respectively (Butler 1998; Dixit and Hering 2003). In the soil and sedimentary environments, inorganic and organic arsenic may be present as salts of available cations, in the form of precipitates or as adsorbates on hydrous oxides, clays, and other surface active materials (Stoeppeler 1992; Francesconi and Kuehnelt 2002; Plant et al. 2005).

Natural processes play important roles in the transport and distribution of trace elements of both natural and anthropogenic origin. Various studies have documented how erosion by wind (Spencer et al. 1995) and water (Hill et al. 1997; De Carlo et al. 2004) can transport substances through the Hawaiian environment. The possibility of transport suggests that the abundance of As in any given location may reflect the transport of materials from more distant sources as well as localized processes. The mobility of arsenic is primarily determined by surface processes such as precipitation, dissolution, adsorption, and desorption. These processes are controlled by geochemical parameters, such as pH, Eh, ionic composition, and mineral type (Masschelein et al. 1991; Bissen and Frimmel 2003; Dixit and Hering 2003).

### 1.3 Arsenic in Hawai‘i

Although environmental concentrations of As in soils have been determined widely throughout the world, ranging from <1 to 95 ppm (Kabata-Pendias 2001), sparse data exist for subtropical volcanic settings. Several recent studies conducted in Hawai‘i determined trace element concentrations, including As, in sediments. Sediment cores were collected from the Ala Wai Canal, an artificial estuary in urban Honolulu on O‘ahu (De Carlo and Spencer 1995; Spencer et al. 1995; De Carlo and Anthony 2002), suspended particulate matter (SPM) and sediments in streams from urban watersheds on O‘ahu (e.g., De Carlo and Spencer 2002; De Carlo et al. 2004, 2005), and soils from agricultural areas on Maui (De Carlo and Dollar 1997). In a single study of aqueous phases, geothermal fluids from the island of Hawai‘i were reported to contain elevated concentrations of As (De Carlo and Thomas 1985). Nonetheless, studies in Hawai‘i that focused specifically on As are very few. Hallacher et al. (1985) examined sediments from Waiākea Mill Pond, the Wailoa River, and Hilo Bay in Hawai‘i to evaluate the extent of contamination resulting from the use of  $\text{As}_2\text{O}_3$  (arsenic(III) oxide) in a canec board manufacturing plant, and more recently, Glendon-Baclig (2007) followed up with a study of speciation in the same locations. In 2012, AECOM Technical Services, Inc., prepared a document for the Hawai‘i Department of Health titled *Hawaiian Islands Soil Metal Background Evaluation Report* (AECOM 2012). For As they reported soil concentrations ranging from 3 to 239 ppm ( $n = 139$ ) with a median concentration of 3.9 ppm. The highest concentrations were reported on the windward side of the island of Hawai‘i in the vicinity of Hilo. In this same area, Cutler et al. (2013) documented As contamination, reaching 880 ppm, in some sugarcane plantation soils.

Unfortunately, the lack of available data over widespread areas of the state has generated substantial disagreement between researchers and regulators regarding the magnitude of natural background levels of As in Hawai‘i and rendered difficult the defining of areas of anthropogenically elevated As concentrations. In light of our earlier findings on the

occurrence of As in sediments and SPM (De Carlo and Spencer 1995; Spencer et al. 1995; De Carlo and Anthony 2002; De Carlo et al. 2004, 2005), some of our more recent findings in marine sediments and biota (UHM 2013) as part of the Ordnance Reef Study, and the association of As with former sugarcane plantation soils (Cutler et al. 2013), we decided that further investigation into the occurrence and distribution of As in the soils and sediments of O‘ahu from a variety of environmental settings was warranted.

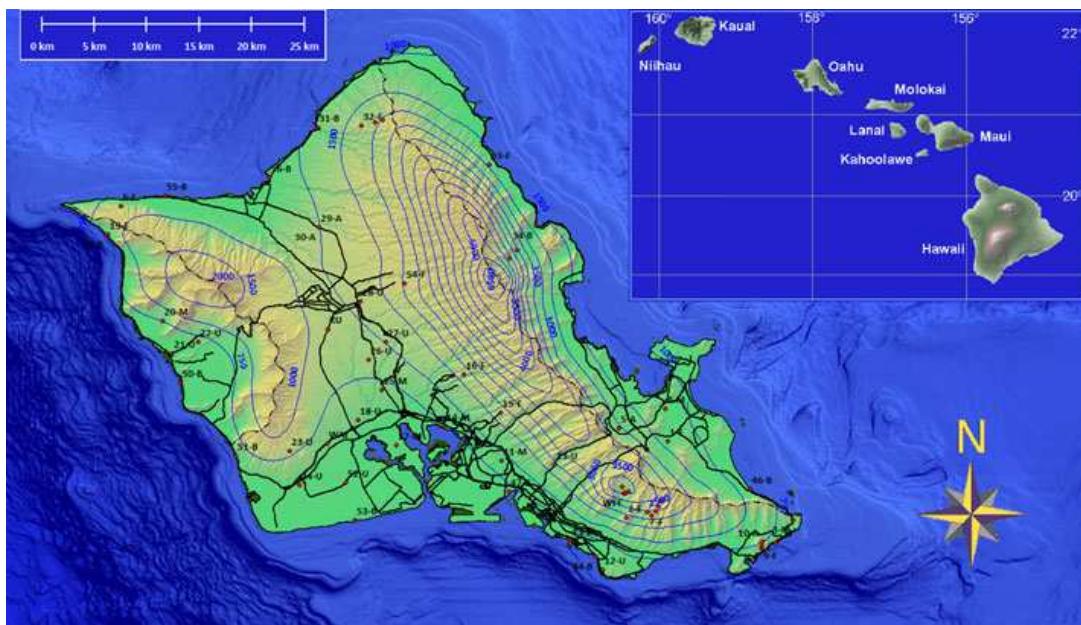
## 2 Methods

### 2.1 Environmental Setting of O‘ahu, Hawai‘i

A very detailed description of O‘ahu, Hawai‘i, is provided in Oki and Brasher (2003); therefore, only a summary of the most relevant information taken from these and other authors will be presented here. O‘ahu is the third largest island ( $1,564 \text{ km}^2$ ) in the Hawaiian archipelago (Fig. 1) and is located between latitude  $21^{\circ}15' \text{ N}$  and  $21^{\circ}45' \text{ N}$  and longitude  $158^{\circ}20' \text{ W}$  and  $157^{\circ}35' \text{ W}$  in the north-central Pacific. The topography of O‘ahu is shaped by the remnants of two shield volcanoes. The older Wai‘anae Volcano in the west and the younger Ko‘olau Volcano in the east formed roughly 3.9 and 2.7 Ma, respectively (MacDonald et al. 1983). Stream, wave, and wind erosion on O‘ahu have caused mass wasting of the shield volcanoes, producing the landscape of steep basaltic mountains, deep valleys, and sheer interfluvial ridges seen today. The Wai‘anae range reaches 1,226 m at its highest point, and the Ko‘olau range reaches 919 m (Stearns 1985). The Schofield Plateau, located between these two mountain ranges, was formed by lavas from the Ko‘olau Volcano banking against the older Wai‘anae Volcano (Stearns 1985). Most of the sugarcane and virtually all of the pineapples grown on O‘ahu were grown on the Schofield Plateau. According to Oki and Brasher (2003), the last two remaining sugarcane plantations on O‘ahu closed in the mid-1990s. Now much of this land is urbanized, used for diversified agriculture, or lies fallow. Two large pineapple plantations continue to operate on the plateau, but like the sugarcane land, some of the pineapple land has undergone residential development. A coastal plain mainly composed of marine sediments and ancient reef deposited on basalt flows at a time of higher sea level surrounds the island (Stearns 1985). It is on this coastal plain that Honolulu, the largest city in Hawai‘i, is situated. According to the 2010 census, the population of Honolulu County was 953,000; the population of urban Honolulu was 337,000. According to Fulton et al. (2001), Honolulu has a population density of 3,054 people/km $^2$ , by far the highest of any US metropolitan area.

The prevalent rock type in Hawai‘i is tholeiitic basalt with a relatively uniform composition, especially when compared to the high degree of variability in rock types typical of continental settings. Although the overall composition of Hawaiian basalt is relatively narrow in range, the trace element content can vary significantly (e.g., Macdonald et al. 1972; Frey et al. 1994). As a result of the abundance of olivine and pyroxene, volcanic rocks in Hawai‘i contain higher concentrations of certain transition elements than continental rocks (Frey et al. 1994). Some of these elements can become further concentrated during soil formation (Li 2000).

Persistent northeasterly trade winds have a strong effect on local climate. The winds carry warm, moist air across the ocean where it encounters the steep windward mountain barrier and is forced to rise. The air cools adiabatically as it rises, and in most cases, the moisture condenses and precipitates on the summits and windward side of the mountain. When the moisture-depleted air moves down the leeward side of the mountains, it warms



**Fig. 1** Terrain map of O'ahu, Hawai'i, showing the 2007–2009 UHM soil and sediment sampling locations. The annual isohyets in millimeters from Giambelluca et al. (2013) are also included

and becomes relatively drier. As a result, little precipitation reaches the leeward side of the mountains. This is reflected in the distribution of rainfall on O'ahu (Fig. 1). The greatest annual rainfall on the island occurs near the crest of the windward Ko'olau range and exceeds 7,000 mm (Giambelluca et al. 2013). In contrast, the maximum annual rainfall in the leeward Wai'anae range reaches just over 2,000 mm, and the leeward coastal areas receive less than 600 mm annually (Giambelluca et al. 2013).

## 2.2 Field and Laboratory Methods

This investigation to augment existing data on the occurrence and distribution of arsenic on O'ahu involved the collection of surface (top 25 cm) soil and beach sediment samples (2006–2007) across O'ahu and the collection of a limited number of cores in 2009, of which the weighted means of the subsamples in the top 20 cm were used for the “surface” As concentration.

A total of 56 soil and sediment samples were collected between July 2006 and May 2007 (Fig. 1). Sample locations were chosen to represent a variety of environments with varying degrees of human impact. Each sample site was categorized as originating from agricultural, urban, forested (conservation), or mixed land use. Land was categorized as agricultural if systematic raising of plants or animals was conducted in the area. Land was categorized as urban if the area was either mainly residential or commercial (this category also includes most parks). Undeveloped sites with little evidence of human impact were classified as forested. Sites with multiple land uses were classified as mixed (this includes golf courses and some areas in the flood plain of streams with agricultural inputs). Beach sands were placed in a separate category. Soils were sampled between 5 and 25 cm depth to avoid root structures and surface debris. Beach sands were collected from the surface near the waterline.

The 2009 sampling (Fig. 1) initially targeted an area that exhibited relatively high SPM As concentrations as part of a first flush during a storm (De Carlo et al. 2004) and exhibited relatively high concentrations of As in stream sediments (De Carlo et al. 2005). This area

along Waiakeakua Stream was located in a forested reach of the stream but also hosts several flower farms. Prior to collecting the core samples in 2009, two surface soil samples (0–20 cm) were collected: One sample was collected in a flower grove, located upstream from the USGS Waiakeakua Stream gage, and another from along the bank of Waihī Stream. Two subsamples were gathered from each site, the first subsample from 0 to 15 cm depth and the second from 15 to 20 cm depth. Soil was collected with a posthole digger and stored into gallon-sized Ziploc® bags. Bags were labeled with the date, location, and soil depth, double bagged, and brought back to the laboratory for processing and analysis. This initial collection provided background information on As levels in the vicinity of the flower farms (Waiakeakua Stream) and solely forested areas (Waihī Stream). The results from the preliminary analysis of these samples were then used to develop hypotheses as to where As-contaminated and noncontaminated surface soils on O‘ahu might be found.

Following the analysis of the preliminary soil samples and the development of hypotheses, a plan was devised to collect soil cores from various environments with potential As contamination. A total of six soil cores were collected from five sites on O‘ahu, Hawai‘i. Four cores were collected in Mānoa Valley: two (WK1 and WK3) from a gardenia farm immediately upstream of the USGS stream gage on the Waiakeakua Stream, one (WK2) from a forested area approximately 350 m up the Waiakeakua Falls trail upstream from the flower farm, and one from 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 former sugarcane field off the H3 highway in Waipahu (WAI). Of these six cores collected, the WK1, WK3, KU, and WAI locations were chosen because of obvious agricultural land use, which suggested long-term use of fertilizer and/or pesticides. The WK2 and LA locations were selected as regions deemed to have experienced limited anthropogenic influence.

Soil cores were collected with a posthole digger. Sections of each core were collected in approximately 10-cm-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. Samples were dried in a laboratory oven at 60 °C to constant weight. Large rocks, roots, and any other debris in the sample were subsequently removed. Samples were subsequently homogenized using either a mortar and pestle or a ball and mill grinder. The color of ground samples was determined using a Munsell chart.

Exactly weighed subsamples of all samples (~0.1 g) were dissolved in sealed Teflon® digestion vessels in a CEM MDS-2100® or MARS EXPRESS® microwave digestion system using a slight modification of the procedure described by Wen et al. (1997). Samples were digested in a strong acid solution using trace metal grade HNO<sub>3</sub>, HCl, and HF. A replicate split of one sample was processed with each batch of digestions. Solid splits of a reference material (NRC Canada MESS-1) and a separate solution containing only acids were also carried through each batch of microwave digestions for quality control purposes. Digested solutions were evaporated to near dryness and the residue re-dissolved and diluted with 2 % (quartz distilled) HNO<sub>3</sub> under a laminar flow hood following trace metal clean procedures. The sample solutions were further diluted with 2 % (v/v) HNO<sub>3</sub> immediately prior to analysis by inductively coupled plasma mass spectrometer (ICPMS) as described by De Carlo et al. (2004).

The abundance of <sup>75</sup>As in digested sample solutions was determined using a VG PQ-2S® quadrupole ICPMS. Calibration was achieved with five aqueous multi-element standards ranging from 0.5 µg/kg to 10 µg/kg of all elements of interest by serial dilutions of a commercially purchased 1,000-µg/kg (SPEX ICPMS-2A mixed metal) stock solution containing natural isotopic abundances of a large suite of elements, including As. A blank

consisting of 2 % (v/v) HNO<sub>3</sub> was used to set the intercept of the calibration. Instrument drift on the ICPMS was monitored using the signal intensity of internal standards <sup>115</sup>In and <sup>209</sup>Bi. Analyte signal intensities were corrected for drift, based on the signal intensities of the internal standards.

Concurrent analysis of reference material solutions (USGS SWRS T-series and digested solutions of NRC Canada MESS-1 estuarine sediment) provided quality control and ensured the accuracy of analytical results. Evaluation of ICPMS data obtained through analysis of standard reference materials over multiple years indicates that the precision of dissolved concentrations >0.1 µg/kg (ppb) is typically better than 10 % relative to isotope masses below 100 atomic mass units, and better than 5–7 % above mass 100. Process blanks ranged between 0.002 and 0.07 ppb, and detection limits were between 0.0005 and 0.08 ppb, depending on the element.

The GIS package Global Mapper 14® was used to plot all sampling locations that were referenced to the World Geodetic System of 1984 (WGS84). The statistical software Minitab 16® was used to calculate descriptive statistics for the surface soil, sediment, and soil core data.

### 3 Results

#### 3.1 Quality Control Data

The elemental concentrations measured in NRC Canada, MESS-1 solutions were compared to the certified mean and 95 % confidence intervals (CI) and are shown in Table 1. Measured As concentrations, in all but one case, always fell within the certified confidence intervals. The difference in concentrations in the diluted solutions we analyzed was only on the order of ~0.2 ppb, well below our lowest calibration standard of 0.5 ppb and similar to concentrations observed in (rinse) water samples inserted between samples.

#### 3.2 Arsenic in Surface Soils and Beach Sediments

A total of 64 surface soil and beach sediment samples, including surface samples and the top intervals of the soil cores, were collected by UHM from 2007 through 2009. The surface data for the two surface samples and six cores collected in 2009 represent weighted means of the subsamples (core intervals) collected between 0 and 20 cm. A statistical summary of the As data from these 64 samples is presented in Fig. 2; the data are included in Table 2. The As concentration ranged from 0.278 ppm to 740 ppm (over four orders of magnitude); the median As concentration was 8.09 ppm. Fifty percent of all As concentrations were between 3.00 and 20.7 ppm (the interquartile range or IQR). It is obvious from the histogram and boxplot in Fig. 2 that the data were not normally distributed; the Anderson–Darling test for a normal distribution supports this observation with a  $p < 0.005$ , thereby rejecting the assumption of normality (Dytham 2011; Ryan et al. 2013).

The As concentrations were also plotted on base maps of O‘ahu and include surface samples (dots) and the top intervals of the soil cores (bulls eyes and small green dots with black outlines; Fig. 3) on which the former sugarcane lands (yellow areas, Fig. 3a) and former and current pineapple lands (green areas, Fig. 3b), as delineated by Oki and Brasher (2003), were overlain. It is readily apparent from these figures that there was no discernible pattern in the As concentrations. By far, the highest As concentrations (>500 ppm) were

**Table 1** Comparison of ICPMS determinations for MESS-1 with NRC Canada-certified values

Standard reference material	As (ppb)
CRM MESS-1 mean	10.6
CRM MESS-1 95 % CI	10.6 ± 1.2
Mean of D1-Mess	<b>8.6</b>
Mean of D2-Mess	10.2
Mean of D3-Mess	10.8
Mean of D4-Mess	10.3
Mean of D5-Mess	10.1
Mean of D6-Mess	10.7
Mean of D7-Mess	11.3
Mean of D8-Mess	10.5
Overall mean	10.3

Concentrations listed in bold fall outside the 95 % CI of the certified mean

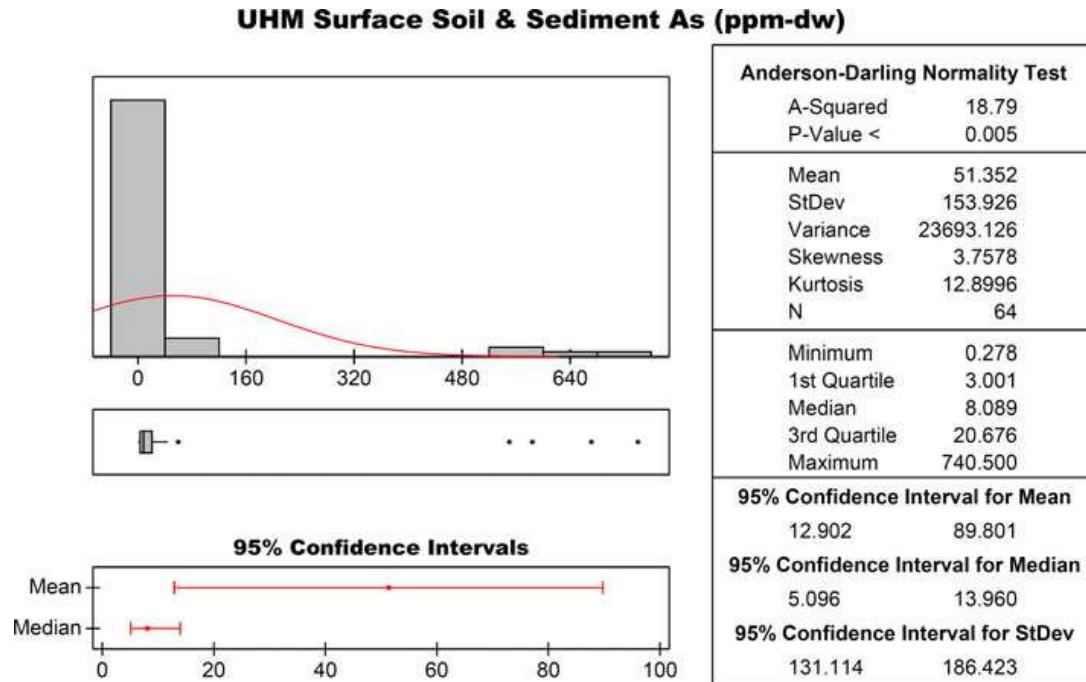
found along Waiakeakua Stream in the upper reaches of Mānoa Valley within and above the flower farms.

According to Bouslog et al. (1994), in the early 1900s, the Hawaiian Sugar Planters Association (HSPA) was interested in developing water supplies for a possible sugarcane plantation in the Mānoa Valley. HSPA purchased 124 acres of land, which today is the Lyon Arboretum owned and operated by UHM, in order to conduct tests of various types of vegetation. HSPA also planted sugarcane test plots in what is now known as Lyon Arboretum (Fig. 4b). So, although there were never sugarcane plantations in the upper Mānoa Valley, there were sugarcane test plots. The one core sample collected from Lyon Arboretum, however, did not have As concentrations >23.0 ppm, well below those reported by Cutler et al. (2013), albeit for full-scale sugarcane plantations on the island of Hawai‘i.

The source of the very high (>500 ppm) As concentrations along Waiakeakua Stream remains uncertain. As mentioned previously, there are flower farms along Waiakeakua Stream where surface As concentrations were as high as 672 ppm. Ironically, higher surface As concentrations (741 ppm) were found in the soil along Waiakeakua Stream above these farms (Fig. 3). It is possible that the high As concentrations are the legacy of earlier applications of an arsenical pesticide instead of or perhaps in addition to more recent application of superphosphate, triple superphosphate, or micronutrient (e.g., Ironite®) fertilizers, all of which are enriched with As, most notably Ironite®.

In those lands identified by Oki and Brasher (2003) as former sugarcane or current and former pineapple plantations (primarily on the Schofield Plateau), only one sample (25-M, mixed agriculture and residential) stands out as being noticeably high in surface As (59.6 ppm). This value, however, is still well below the surface As concentrations observed along Waiakeakua Stream in the Mānoa Valley and former sugarcane lands on the island of Hawai‘i (Cutler et al. 2013). Aside from the samples along Waiakeakua Stream, the six highest surface As concentrations on O‘ahu (Fig. 3) occurred at Central O‘ahu Regional Park, Waikele (Site 25-M, 59.6 ppm); Pūpūkea Paumalū Forest Preserve (32-F, 44.5 ppm); Kawailoa Forest Preserve, Wahiawā (54-F, 43.9 ppm); Neal Blaisdell Park, Waimalu (14-M, 30.1 ppm); Kīpapa Community Park, Mililani Town (27-U, 26.7 ppm); and Waipi‘o Soccer Complex (17-M, 26.6 ppm). Of these six sites, half are not associated with prior plantation agriculture as mapped by Oki and Brasher (2003).

Boxplots of the surface soil and sediment As concentrations (Fig. 5) indicate that the distribution of As differs between land uses. In fact, the nonparametric Kruskal–Wallis test



**Fig. 2** Minitab 16® statistical summary of As data from 2007 to 2009 surface soil and sediment sampling including a histogram with normal distribution indicated with red line, boxplot, median and mean with 95 % confidence intervals, and various descriptive statistics.  $p < 0.005$  in the Anderson–Darling normality test rejects the hypothesis that the data are normally distributed

indicated that at least one pair of the medians differed significantly from the other medians at  $\alpha = 0.05$  ( $p = 0.006$ ). A series of Mann–Whitney  $U$  tests between the various land use pairs indicated that the median beach As concentration (2.75 ppm) was significantly different ( $\alpha = 0.05$ ) from the median As concentrations for the other land uses. Summary statistics by land use and overall are presented in Table 3. Although the median beach As concentration was the lowest for all land uses, the minimum beach As concentration (1.99 ppm) was not the lowest measured overall. Lower As concentrations were detected in forested (three with a minimum = 0.300 ppm) and urban (one with a minimum = 1.67 ppm) areas. The median As concentrations sorted by land use were beach (2.75 ppm) < urban (9.09 ppm) < forested (9.20 ppm) < mixed (19.6 ppm) < agriculture (21.8 ppm).

In Fig. 3, we also included surface soil As data collected by the Hawai‘i Department of Health (HDOH, triangles) and the Natural Resources Conservation Service (NRCS, diamonds) on O‘ahu, in addition to our surface soil and sediment data. These data were reported in Appendix B of AECOM (2012). A notably high concentration (58 ppm) of As was found by HDOH in the Kahana Valley. It should be noted that HDOH actually collected two samples with identical decimal degree coordinates out to five decimal places. One sample was 47 ppm and the other 58 ppm, the highest of 19 samples collected by HDOH on O‘ahu. Again, these higher concentrations could be the legacy of arsenical pesticides and/or more recent fertilizer use. Of the 10 soil As concentrations reported by NRCS, the highest was 23.3 ppm on agricultural land in Waipahu, which was former sugarcane land.

Finally, in Fig. 3, we included the As data from the 24 USGS NAWQA stream sediment samples collected on O‘ahu (De Carlo et al. 2005, squares). The statistical summary of these data is presented in Fig. 6 and Table 4 (by land use and overall). Like our soil and more recent beach sediment data, the As concentrations were not normally distributed. The

**Table 2** Surface (top 20–25 cm) soil and sediment As concentrations (ppm-dw)

Sample ID	Sampling date	Latitude (N)	Longitude (W)	Land use <sup>b</sup>	As
1	07/24/06	21.37299	-157.76292	F	0.278
2	07/25/06	21.30759	-157.79858	F	15.4
3	07/25/06	21.30497	-157.65544	M	3.49
4	07/25/06	21.40058	-157.76529	M	5.78
5	07/25/06	21.38404	-157.80458	A	13.3
6	07/29/06	21.57355	-158.23024	F	3.98
7	07/31/06	21.31221	-157.78024	F	13.4
8	09/02/06	21.28075	-157.68264	F	1.24
9	09/02/06	21.28303	-157.68264	F	4.29
10	09/02/06	21.28606	-157.68219	A	3.00
11	09/02/06	21.35583	-157.90500	M	19.6
12	09/03/06	21.26266	-157.81865	U	8.07
13	09/03/06	21.35252	-157.86002	U	20.8
14	09/03/06	21.38511	-157.95354	M	30.1
15	09/03/06	21.39709	-157.90555	F	19.1
16	09/03/06	21.42986	-157.93669	F	2.66
17	09/04/06	21.36907	-157.99483	M	26.6
18	09/04/06	21.39087	-158.02765	U	1.67
19	09/04/06	21.54918	-158.24127	F	9.19
20	09/04/06	21.47500	-158.19443	M	4.88
21	09/04/06	21.44819	-158.18658	U	8.11
22	09/04/06	21.45802	-158.16420	U	17.5
23	09/04/06	21.36438	-158.08635	U	3.83
24	09/04/06	21.33503	-158.07785	U	16.8
25	09/05/06	21.41689	-158.00728	M	59.6
26	09/05/06	21.44245	-158.01855	U	9.09
27	09/05/06	21.45766	-158.00383	U	26.7
28	09/05/06	21.49164	-158.02559	U	16.8
29	09/05/06	21.55531	-158.06100	A	21.8
30	09/05/06	21.55517	-158.06096	A	12.6
31	09/05/06	21.64068	-158.06233	B	5.08
32	09/05/06	21.64210	-158.02496	F	44.5
33	09/05/06	21.60858	-157.91577	F	10.6
34	09/05/06	21.55638	-157.87547	B	16.8
35	04/14/07	21.32160	-157.76909	F	7.87
36	04/14/07	21.31669	-157.77101	F	5.81
37	04/14/07	21.31311	-157.77307	F	2.12
38	04/14/07	21.30921	-157.77667	F	1.43
39	05/05/07	21.64484	-158.01305	F	8.21
40	05/05/07	21.64690	-158.00693	F	2.27
41	05/06/07	21.53538	-157.89204	F	20.4
42	05/06/07	21.52879	-157.89829	F	6.60
43	05/19/07	21.28796	-157.84642	B	1.99

**Table 2** continued

Sample ID	Sampling date	Latitude (N)	Longitude (W)	Land use <sup>b</sup>	As
44	05/19/07	21.27400	-157.82434	B	2.58
45	05/23/07	21.28569	-157.67137	B	3.01
46	05/23/07	21.33154	-157.69286	B	2.66
47	05/23/07	21.32942	-157.89864	B	2.13
48	05/23/07	21.30108	-157.87703	B	5.10
49	05/24/07	21.54911	-158.24236	B	2.80
50	05/24/07	21.42316	-158.17908	B	2.51
51	05/24/07	21.35994	-158.13197	B	3.28
52	05/24/07	21.33747	-158.03813	U	7.89
53	05/24/07	21.30513	-158.03035	B	2.12
54	05/27/07	21.50733	-157.98804	F	43.9
55	05/27/07	21.58228	-158.19263	B	2.70
56	05/27/07	21.59796	-158.10349	B	6.14
WFF <sup>a</sup>	03-Feb-09	21.32846	-157.79940	A	550
WSB <sup>a</sup>	03-Feb-09	21.32830	-157.80080	F	30.2
WK1 <sup>a</sup>	10-Mar-09	21.32854	-157.79936	F <sup>c, e</sup>	584
WK2 <sup>a</sup>	10-Mar-09	21.32969	-157.79625	F	741
WK3 <sup>a</sup>	12-Sep-09	21.32855	-157.79933	F <sup>c</sup>	672
LA <sup>a</sup>	10-Mar-09	21.33384	-157.80177	F <sup>c</sup>	23.0
WAI <sup>a</sup>	16-Aug-09	21.37061	-158.05423	A	44.0
KU <sup>a</sup>	16-Aug-09	21.46806	-158.05339	A	23.4

ppm-dw part per million-dry weight

<sup>a</sup> Weighted mean of top 20 cm of core

<sup>b</sup> Land use: *F* forested, *A* agricultural, *U* urban, *M* mixed agricultural and urban/residential, *B* beach

<sup>c</sup> Nursery or gardens surrounded by forested (conservation lands)

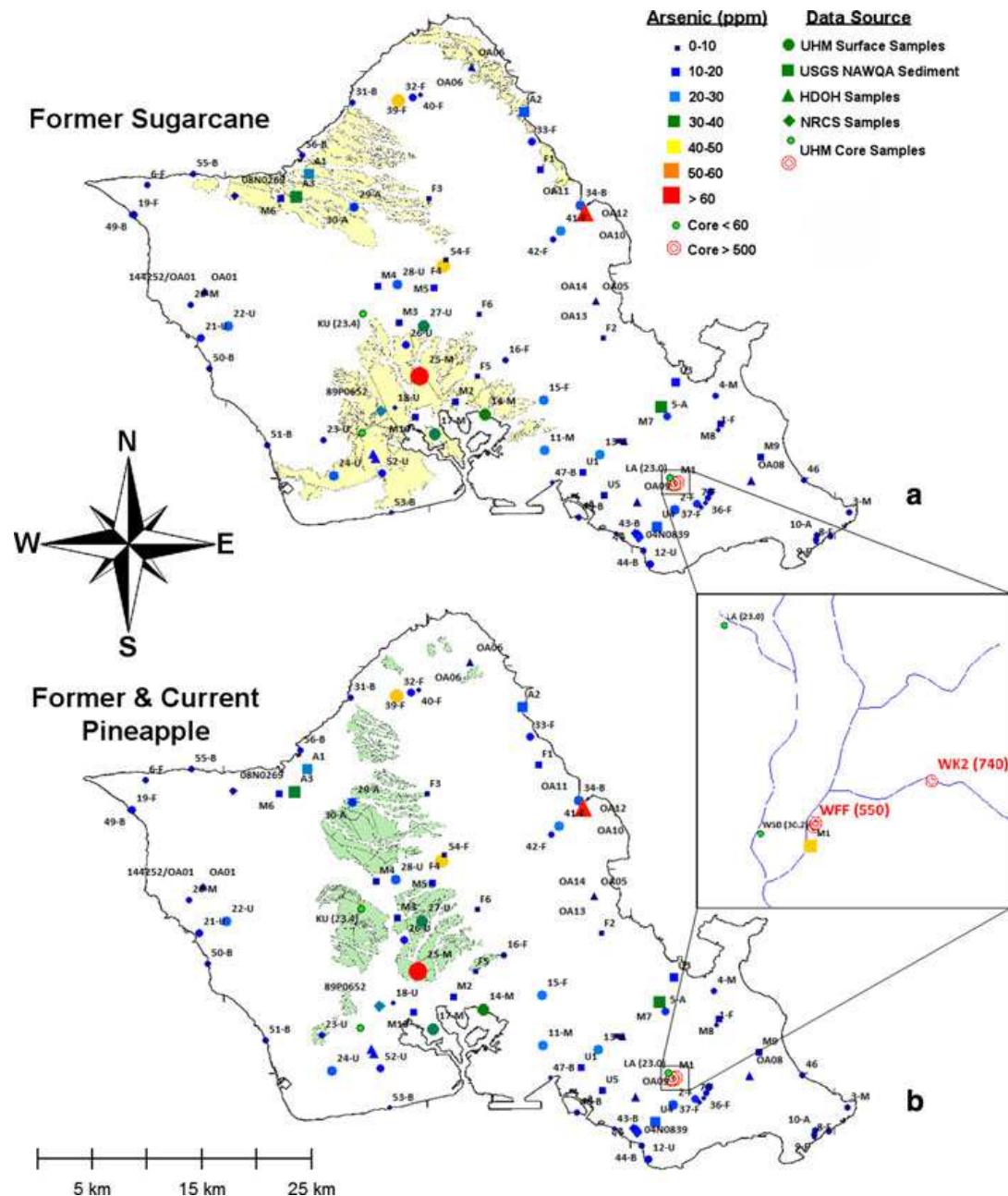
<sup>d</sup> USGS during their NAWQA studies labeled this site “*M*” for mixed

As concentration in the NAWQA sediments ranged from 1.0 to 44 ppm with an overall median concentration of 6.1 ppm; the median concentrations by land use were forested (1.7 ppm) < mixed (6.1 ppm) < urban (6.6 ppm) < agriculture (22 ppm), again with the highest median value associated with agricultural land use.

Not surprisingly, particularly in light of our more recent soil As findings, the highest stream sediment As concentration found during the NAWQA study was 44 ppm for sediment collected in Waiakeakua Stream below the flower farms and the USGS stream gage. The land use for this particular sample was labeled “mixed” during the NAWQA study although it is above the residential development but downstream of the flower farms. In our more recent investigations, the land use in this area was considered forested because forested conservation lands surround the sample sites.

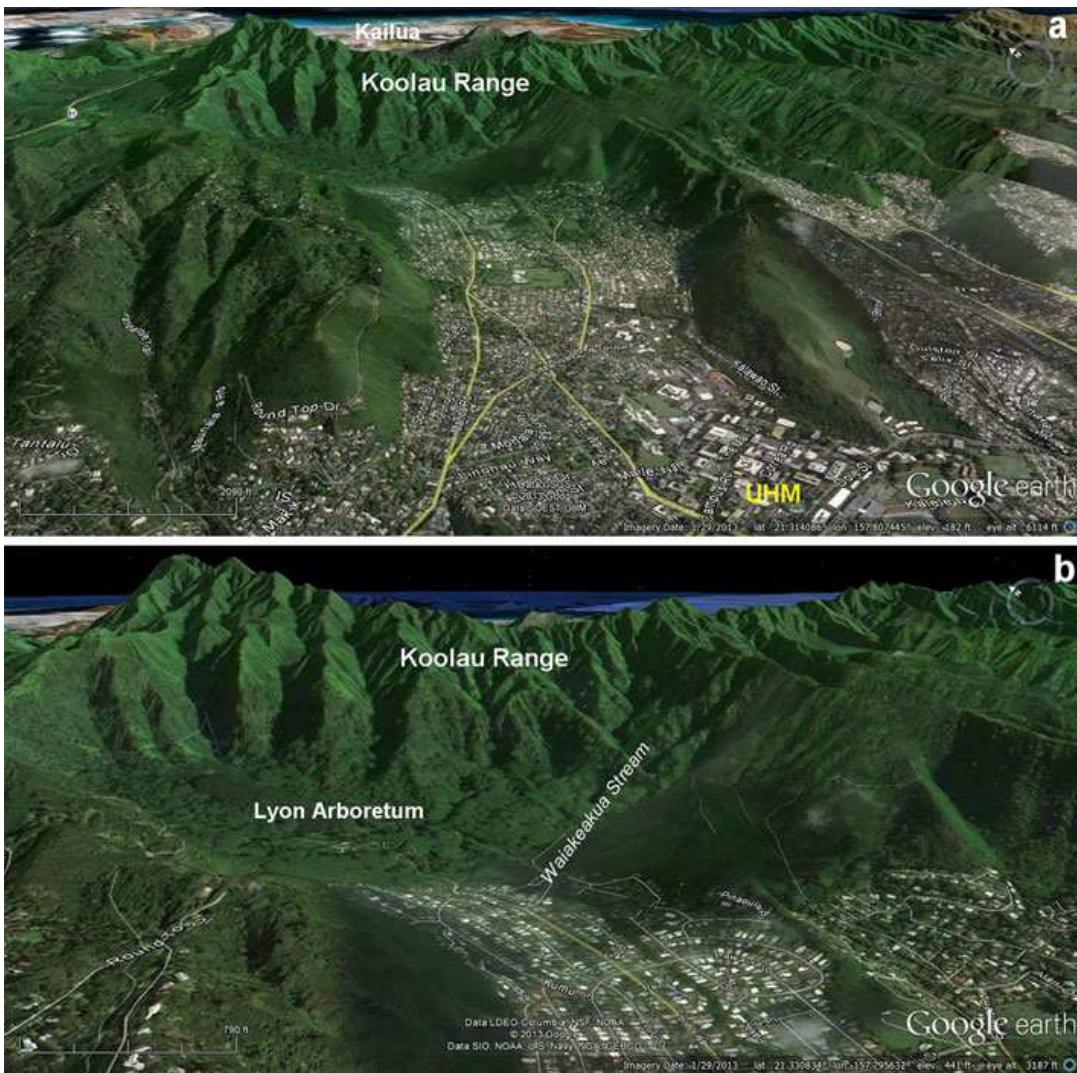
### 3.3 Arsenic in Soil Cores

A total of six cores plus two surface samples (separated into two vertical subsamples) were collected in different land use areas of O‘ahu in order to understand better the vertical distribution of As in soils. The data from these samples were used to create vertical profile



**Fig. 3** Plot of surface soil and sediment arsenic (As) concentrations in parts per million-dry weight (ppm-dw) for the 2007–2009 samplings compared with NAWQA sediment data (De Carlo et al. 2005) and HDOH samples (HDOH 2012). The surface As concentration for 2009 cores (bulls eyes and green dots) represents weighted means of the top 20 cm of the core. The *inset* shows in greater detail the distribution of As from samples collected along Waiakeakua Stream. The former sugarcane land (**a**) and former and current pineapple land (**b**) from Oki and Brasher (2003) have been overlaid on the map of O'ahu, Hawai'i

plots of As concentration for each sampling location (Table 5 and Fig. 7). The plots show that for those sites with elevated concentrations of As (WFF, WK1, WK2, and WK3), As is somewhat depleted in the top ~5 cm with values from 100 to 300 ppm lower than the highest concentrations at depth. The maximum As concentrations in the three cores from the banks of Waiakeakua Stream range from 615 to 913 ppm with the highest concentration occurring at WK2, which was situated in the forest above the flower farms.



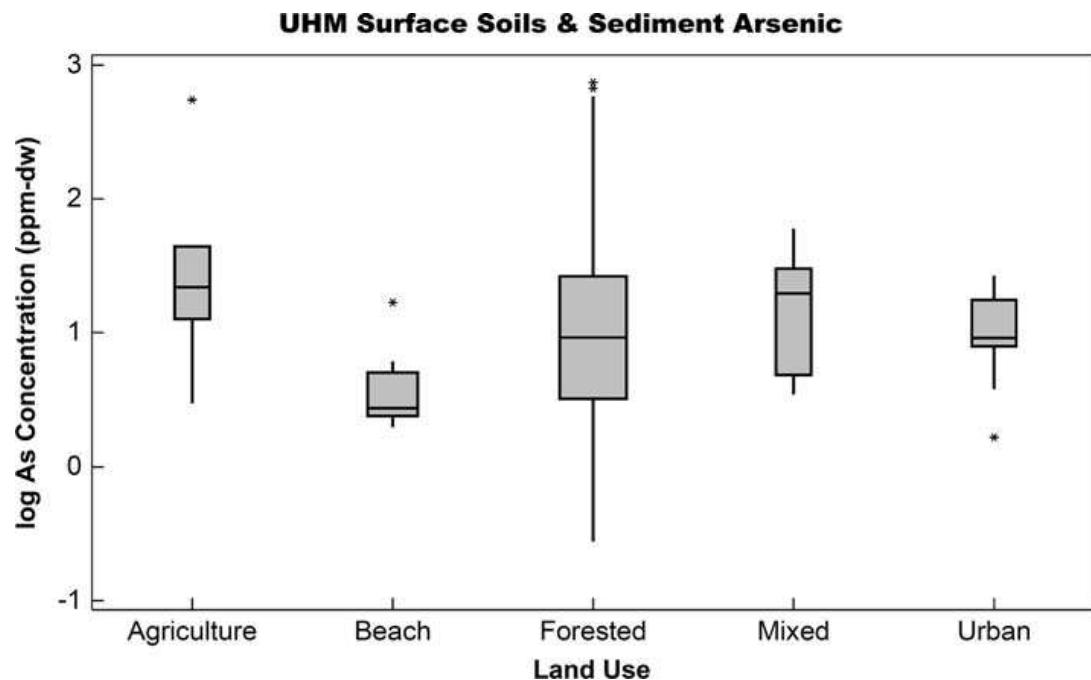
**Fig. 4** Oblique aerial images from Google Earth® showing the entire Mānoa Valley (a) and the head of Mānoa Valley where Waiakeakua Stream and the Lyon Arboretum are located

The fact that As concentrations were elevated for all core samples is readily apparent in Fig. 7 with the lowest concentration (17.8 ppm at WAI) well above the overall surface As median for the soils and beach sediments (8.09 ppm). In fact, with the exception of the 17.8-ppm minimum, all soil profile concentrations exceeded the highest surface median, i.e., agriculture at 21.8 ppm. This is readily apparent for the data from WSB, LA, WAI, and KU presented in Table 5.

## 4 Discussion

### 4.1 Comparison of O'ahu Arsenic Concentrations with Other Locations

In Table 6, we compare the As concentrations measured in surface soils and beach sediments during this recent investigation (first row of data), with our earlier investigations and the results of others worldwide. Reimann et al. (2009) provide a more comprehensive

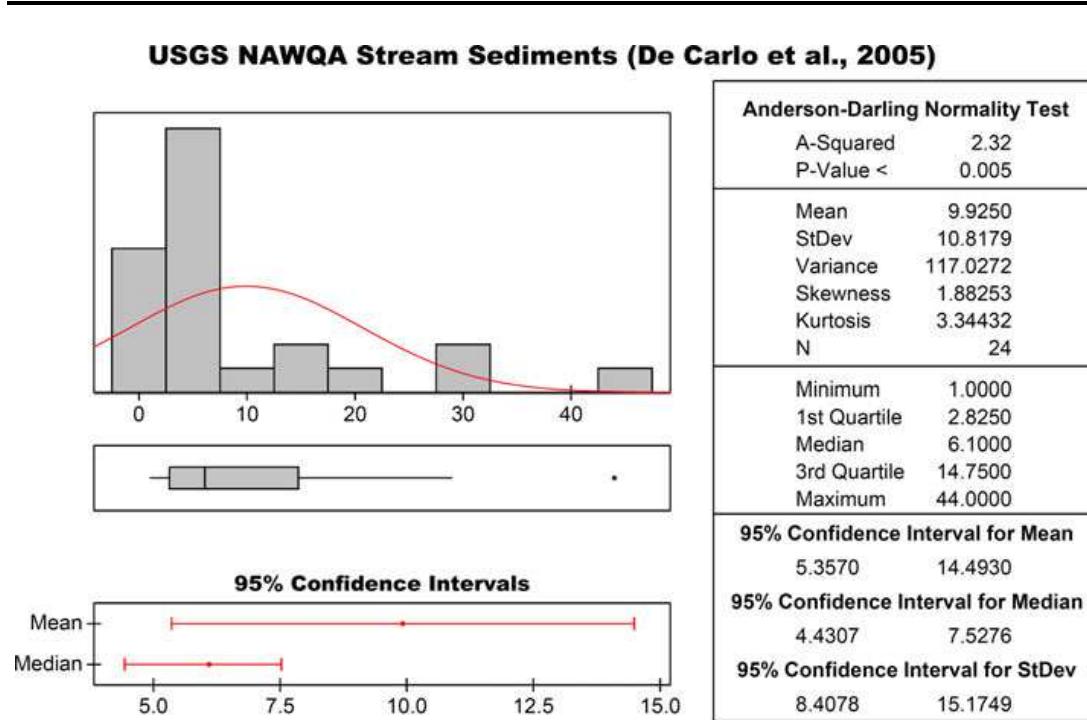


**Fig. 5** Standard boxplots of As data from the 2007–2009 surface soil and sediment sampling broken out by land use. It was necessary to use a log (base 10) concentration axis, because the As concentrations range over four orders of magnitude. Only the median As concentration for beach sediment was statistically different ( $\alpha = 0.05$ ) from the other land use medians

**Table 3** Statistical summary of As data from the UHM surface soil and sediment sampling by land use

Land use	Agriculture	Beach	Forested	Mixed	Urban	Overall
Maximum	550	16.8	741	59.6	26.7	741
3rd quartile	44.0	5.09	26.6	30.1	17.5	20.7
Median	21.8	2.75	9.20	19.6	9.09	8.10
1st quartile	12.6	2.42	3.30	4.88	7.89	3.00
Minimum	3.00	1.99	0.300	3.49	1.67	0.300
Mean	95.4	4.21	90.9	21.4	12.5	51.4
SE mean	75.9	1.03	43.6	7.57	2.33	19.2
SD	201	3.84	218	20.0	7.72	154
N	7	14	25	7	11	64
Missing	0	0	0	0	0	0

summary table (their Table 1) listing the median concentrations for a variety of media. We agree with Reimann and de Caritat (1998) that “...chemical composition of natural materials seldom displays a normal distribution [and] ... The median value (50th percentile) is a much more robust descriptor of non-normally distributed, strongly skewed populations, than the mean.” Therefore, whenever possible, we report median value or an estimate of the median based on the reported mean and variance, assuming a lognormal distribution, which is not necessarily true but better than assuming a normal distribution. We used a median estimator suggested by Helsel (personal communication 2013):



**Fig. 6** Minitab 16® statistical summary of As data from USGS NAWQA stream sediment sampling (De Carlo et al. 2005) including a histogram with normal distribution indicated with red line, boxplot, median, and mean with 95 % confidence intervals, and various descriptive statistics.  $p < 0.005$  in the Anderson–Darling normality test rejects the hypothesis that the data are normally distributed

**Table 4** Statistical summary of As data from the USGS NAWQA study of stream sediments (De Carlo et al. 2005)

Land use	Agriculture	Forested	Mixed	Urban	Overall
Maximum	28	6.4	44 <sup>a</sup>	16	44
3rd quartile	28	3.3	12	14	15
Median	22	1.7	6.1	6.6	6.1
1st quartile	16	1.2	5.0	3.5	2.8
Minimum	16	1.0	4.1	2.4	1.0
Mean	22	2.4	12	8.1	9.9
SE mean	3.5	0.83	4.3	2.4	2.2
SD	6	2.0	14	5.4	11
N	3	6	10	5	24
Missing	0	0	0	0	0

<sup>a</sup> Although downstream of the flower farms, we labeled the land use *F* for forested for our soil samples

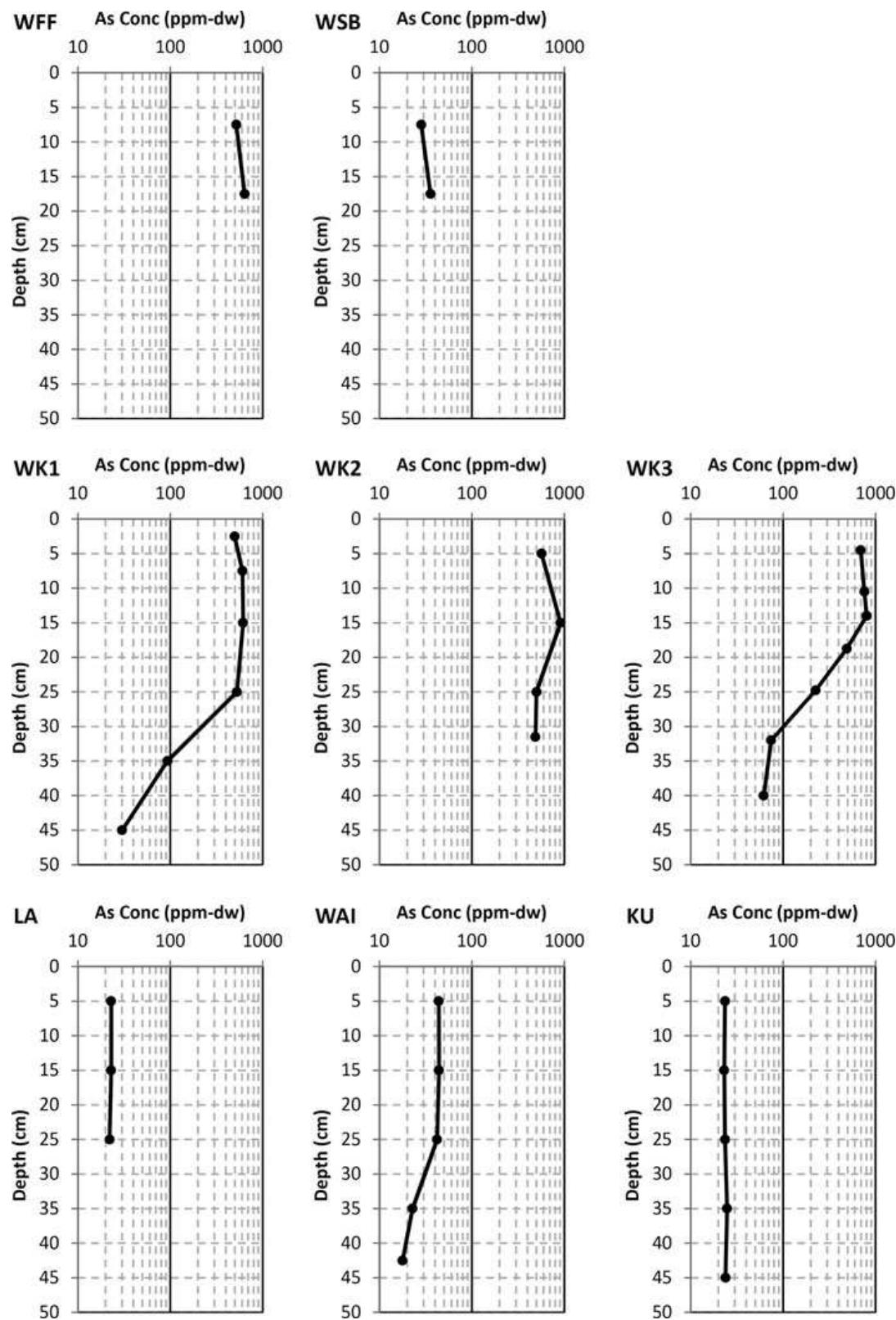
$$Md = \frac{Mn}{e^{(0.5 \times \ln[Var])}}$$

where  $Md$  = median,  $Mn$  = mean, and  $Var$  = variance, i.e.,  $SD^2$ . If we did not have enough information to estimate a median, we presented the mean but clearly flagged the value as a mean and not a median.

**Table 5** O‘ahu soil cores collected in 2009

ID	Lat (N)	Lon (W)	Date (HST)	Depth interval (cm)	As (ppm)
WFF	21.32846	−157.79940	03-Feb-09	0–15	520
				15–20	641
WSB	21.32830	−157.80080	03-Feb-09	0–15	28.4
				15–20	35.7
WK1	21.32854	−157.79936	10-Mar-09	0–5	499
				5–10	607
				10–20	615
				20–30	528
				30–40	93.4
				40–50	30.2
WK2	21.32969	−157.79625	10-Mar-09	0–10	568
				10–20	913
				20–30	502
				30–33	489
WK3	21.32855	−157.79933	12-Sep-09	0–9	694
				9–12	759
				12–16	805
				16–21.5	490
				21.5–28	226
				28–36	74.3
				36–44	61.8
				0–10	23.0
LA	21.33384	−157.80177	10-Mar-09	10–20	23.0
				20–30	22.1
				0–10	43.8
WAI	21.37061	−158.05423	16-Aug-09	10–20	44.1
				20–30	42.1
				30–40	22.8
				40–45	17.8
				0–10	23.6
KU	21.46806	−158.05339	16-Aug-09	10–20	23.1
				20–30	23.6
				30–40	24.8
				40–50	23.9

It is readily apparent from Table 6 that our median As concentration for surface soil and sediment from our 2007–2009 sampling is above a number of median values for other locations. Nonetheless, with the exception of the As measured in the soils along Wai-akeakua Stream, our As concentrations in surface soils and sediments were relatively low (<60 ppm) when compared with the values reported by Cutler et al. (2013) for former sugarcane lands on the island of Hawai‘i. Cutler et al. (2013) reported mean values of  $280 \pm 190$  ppm with 190 representing one standard deviation (SD); the estimated median



**Fig. 7** Vertical profile plots of arsenic (As) concentration in parts per million-dry weight (ppm-dw)

for these data was  $\sim 230$  ppm. Cutler et al. (2013) also reported that *background* As concentrations in soils not used for sugarcane were all  $<20$  ppm, which is certainly comparable to our overall surface soil median value of 8.09 ppm. We did not, however, consistently see the elevated As concentrations reported by Cutler et al. (2013) for former sugarcane land. One possible confounding factor for the data collected on the island of Hawai‘i was the fact that these lands are downwind from an oil-fired power plant located to the south of Hilo. Certainly, the pattern of Cutler et al.’s (2013) As (high values inside the sugarcane lands and low values outside of these lands) suggests that it is indeed activities related to sugarcane agriculture; however, the impact of the power plant cannot be entirely dismissed. According to Pacyna (1987), oil has about 80 times less As than coal, but is still considered rich in As.

Our surface soil and sediment median of 8.09 ppm is higher than the median As concentration reported for agricultural lands in Canada (6.6 ppm, Reimann and de Caritat 1998). This is rather remarkable given that our median value was “diluted” with the inclusion of beach sand (median = 2.75 ppm). The median As concentration for lands designated as agricultural was 21.8 ppm based on a total of seven samples. Again, still well below the median estimated from Cutler et al.’s (2013) data but well above the As median for other agricultural soils reported in Table 6. Kabata-Pendias (2001) did report As concentrations ranging from 31 to 625 ppm for soils contaminated with arsenical pesticides. Certainly, this agrees well with Cutler et al.’s (2013) findings but does not explain why most of the values we measured in 2007–2009 were relatively low.

Reimann et al. (2009) in their article titled *Arsenic distribution in the environment: The effects of scale* may have an explanation. They examined As concentrations in a variety of media at scales ranging from local ( $0.5\text{--}500\text{ km}^2$ ) to continental ( $0.5\text{--}50\text{ million km}^2$ ) and concluded that “[a] high sample density is needed to reliably detect mineralization or contamination in soil samples.” In the case of mineral exploration (e.g., using As to locate Au deposits), by high, Reimann et al. (2009) referred to densities on the order of “...one sample per  $1\text{--}5\text{ km}^2$  in the reconnaissance phase (e.g., stream sediments) and up to several hundred samples per  $\text{km}^2$  in the follow-up and target phases (most often soils) are routinely used.” For assessing As contamination at a regional scale ( $500\text{--}500,000\text{ km}^2$ ), Reimann et al. (2009) report sampling densities ranging from one sample/ $\text{km}^2$  to one sample/ $300\text{ km}^2$ . Therefore, for O‘ahu, the number of samples required to assess As contamination might need to be as high as 1,570. Certainly, Cutler et al.’s (2013) sampling density was higher than the sampling density to date on O‘ahu.

The median As concentration reported by De Carlo et al. (2005) in streambed sediments on O‘ahu (6.1 ppm,  $n = 24$ ) from the USGS NAWQA data compares well with the overall median As concentration for streambed sediments reported by Rice (1999) for the conterminous USA (6.3 ppm,  $n = 541$ ). It is interesting to note, however, that our median As concentration for marine sediments in the coastal waters off western O‘ahu, as part of the Ordnance Reef Study (UHM 2013) of 8.6 ppm, was higher. This is not altogether surprising given that a number of authors have noted that As is naturally enriched in the marine environment (Francesconi and Edmonds 1998; Maher and Butler 1988; Reimann et al. 2009). In fact, Francesconi and Edmonds (1998) reported that over 100 years ago high concentrations of As in marine samples were known to exist. Maher and Butler (1988) report that “[a]rsenic concentrations in near-shore unpolluted marine sediments are normally between 0.1 and 50 [ppm] [and that] ...[i]n sediments subject to anthropogenic inputs, especially from mines and smelters, the arsenic content can exceed 1,000 [ppm].” The As concentrations for the Ordnance Reef samples (UHM 2010) fall within the *normal* range. Similarly, the As values obtained from two cores in the Ala Wai Canal (De Carlo

**Table 6** Statistical comparison of arsenic (As) from our recent investigation of surface soils and sediments on O‘ahu, Hawai‘i, with other investigations in Hawai‘i and worldwide; concentrations are in parts per million (ppm)

	As concentration			
	Min	Median	Max	n
2007–2009 O‘ahu surface soils and sediments	0.278	8.09	740	64
Ordnance Reef Study marine sediments <sup>c</sup>	0.200	8.60	43.9	75
Island of Hawai‘i former sugarcane land <sup>d</sup>	39	230 <sup>a</sup>	880	100
NAWQA O‘ahu stream sediments <sup>e</sup>	1.0	6.1	44	24
Ala Wai Canal sediment cores <sup>f</sup>	6.20	17.9	30.1	73
World <sup>g</sup>	–	5 <sup>a</sup>	–	
Kola project topsoil (0–5 cm) <sup>g</sup>	<0.05	<0.05	16	
Canada agricultural soils (Ap horizon) <sup>g</sup>	0.2	6.6	19	
Finland agricultural soil—(0–25 cm) <sup>g</sup>	<0.2	1.55	13.4	
Norway, Trondheim, urban soil (0–2 cm) <sup>g</sup>	–	0.5	83	
Australia laterite soils (25 ± 15 cm) <sup>g</sup>	<0.5	3	170	
Austria stream sediments <sup>g</sup>	<2	2	1,305	
Southern Scotland stream sediments <sup>g</sup>	<4	12	150	
Harz, Germany stream sediments <sup>g</sup>	<5	22	334	
Norway overbank sediments <sup>g</sup>	<0.05	5.3	57.6	
Total content in soils <sup>g</sup>	0.1	3.6–8.8 <sup>b</sup>	48	
US Histosols <sup>i</sup>	<0.1	5 <sup>b</sup>	48	
US forest soils <sup>i</sup>	<0.1	7 <sup>b</sup>	93	
US loamy and clay soils <sup>i</sup>	1.7	7.7 <sup>b</sup>	27	
Thailand loamy and clay soils <sup>i</sup>	7.2	12.8 <sup>b</sup>	18.4	
US Podzols and sandy soils <sup>i</sup>	<0.1	5.1 <sup>b</sup>	30	
US soils, arsenical pesticide contamination <sup>i</sup>	31	–	625	
Mafic rocks (basalts, gabbros) <sup>i</sup>	0.6	–	2.0	
Conterminous US streambed sediments <sup>j</sup>	1	6.3	200	541
Upper continental crust <sup>k</sup>		2.0 <sup>b</sup>		
Lower continental crust <sup>k</sup>		1.3 <sup>b</sup>		

<sup>a</sup> Estimated

<sup>b</sup> Mean

<sup>c</sup> UHM (2010)

<sup>d</sup> Cutler et al. (2013)

<sup>e</sup> De Carlo et al. (2005)

<sup>f</sup> De Carlo and Anthony (2002), two cores subsampled at 2–4-cm-depth intervals

<sup>g</sup> Reimann and de Caritat (1998)

<sup>h</sup> Pais and Jones (1997)

<sup>i</sup> Kabata-Pendias (2001)

<sup>j</sup> Rice (1999)

<sup>k</sup> Wedepohl (1995)

and Anthony 2002) which ranged from 6.20 to 30.1 ppm (median = 17.9 ppm) fall within the normal range as well. Hallacher et al. (1985) reported 34 and 56 ppm As in two samples collected from the top 3–5 cm of sediment in Hilo Bay; the bottom (>50 cm) As

concentrations for these same cores were 63 and 19 ppm, respectively. These results are not surprising given Hallacher et al. (1985) noted that “[t]he bay and adjoining Wailoa River estuary system are severely polluted with arsenic as a result of dumping of arsenic trioxide (used as an antitermite agent) into the Waiākea Mill Pond and Wailoa River by a canec (a building material made from sugarcane waste) manufacturing plant during the years 1932–1963.”

As for the transport of As, the data from our cores WFF, WK1, WK2, and WK3 (Fig. 7 and Table 5) provide some clues. The As concentrations in these cores were somewhat depleted in the top ~5 cm with values from 100 to 300 ppm lower than the highest concentrations at depth. The surface depletion of As in samples collected from the soils along Waiakeakua Stream may, in part, have been caused by surface leaching of As. This process, however, would be slow given that these top-most soil layers were, in all likelihood, oxic. While As in minerals is readily soluble, its migration in soils is limited by strong sorption to clays, oxyhydroxides, and organic matter (Fuller et al. 1993; Kabata-Pendias 2001; Dixit and Hering 2003). Therefore, As, whether geogenic or anthropogenic, when released, generally will not migrate far, particularly under oxic conditions.

#### 4.2 Comparison of O’ahu Arsenic Concentrations with Environmental Guidelines

Environmental Quality Guidelines (EQGs) for soils and sediments are presented in Table 7. The median As concentration in soils from forested (conservation) lands (9.19 ppm,  $n = 25$ ) and urban (residential) lands (9.09 ppm,  $n = 11$ ) was lower than the HDOH soil environmental action level (EAL) for Hawai‘i (24 ppm) and even lower than the CCME soil EQG of 12 ppm for all land uses (Table 5); the median As concentrations in soils from agricultural lands (21.8 ppm,  $n = 7$ ) and mixed lands (19.6 ppm,  $n = 7$ ) exceeded the CCME soil EQG but was still below the HDOH soil action level of 24 ppm. A total of 12 out of 50 (24 %) soil samples collected in this research exceed the HDOH soil EAL for As.

The median As concentration in beach sands (2.75 ppm) falls below the NOAA marine sediment threshold effects level (TEL, also known as the CCME Interim Sediment Quality Guideline or ISQG) of 7.24 ppm; only one of 14 (7.1 %) of beach sand samples collected in this research exceeds the NOAA marine sediment TEL for As. This, however, was not the case for the marine sediments collected during the 2009 Ordnance Reef Study (UHM 2010). In this case, 42 out of 76 (55 %) of the As concentrations in the sediment samples exceeded the NOAA marine sediment TEL of 7.24 ppm, and four of the Ordnance Reef samples exceeded the NOAA marine sediment probable effect level (PEL, also known as the CCME marine sediment PEL) of 41.6 ppm. It is not surprising that the beach sediment (sand) was lower in As. These sediments are being continuously reworked by wave action, and much of the fine sediment including the clays, oxyhydroxide particles, and organic particles have been removed. It is these particles to which As would adhere. Both Yan-Chu (1994) and Inskeep et al. (2002) discuss the forms of As in soils and sediments and the factors affecting the As concentration. According to Inskeep et al. (2002), arsenate has a strong affinity of metal oxyhydroxides and clay minerals; arsenite is more selective, preferring iron oxyhydroxides. They go on to state that “...the sorption of arsenate and arsenite by Fe(III)-oxide solid phases is perhaps *one of the most important sinks for As in aquatic and terrestrial environments* [emphasis added].” Yan-Chu (1994) reported that arsenic content correlated negatively with sand, but positively with clay content. Yan-Chu (1994) goes on to say that “[a]rsenic occurs mainly as inorganic species but also can be bound to organic material in soils.” According to ATSDR (2007), As in soil is positively

**Table 7** Various Environmental Quality Guidelines (EQGs) for arsenic (As) with concentrations in parts per million-dry weight (ppm-dw) in various media

Environmental quality guideline	As
Freshwater and marine sediment quality guidelines	
NOAA SQuiRTs freshwater TEL (also known as the CCME freshwater ISQG)	5.90
NOAA SQuiRTs freshwater PEL (also known as the CCME freshwater PEL)	17.0
NOAA SQuiRTs marine TEL (also known as the CCME marine ISQG)	7.24
NOAA SQuiRTs marine PEL (also known as the CCME marine PEL)	41.6
Soil quality guidelines	
HDOH soil EAL	24
CCME agricultural land use	12
CCME residential/park land use	12
CCME commercial land use	12
CCME industrial land use	12
USEPA RSL for resident soil	0.61
USEPA RSL for industrial soil	2.4

NOAA National Oceanic and Atmospheric Administration, *SQuiRTs* Screening Quick Reference Tables (Buchman 2008), *TEL* threshold effects level, *PEL* probable effects level, *CCME* Canadian Council of Ministers of the Environment (CCME 2013), *ISQG* Interim Sediment Quality Guideline, *PEL* probable effect level, *HDOH* Hawai'i Department of Health, *EAL* environmental action level, *USEPA* US Environmental Protection Agency, *RSL* regional screening level (USEPA 2013)

correlated to clay, organic carbon, cation exchange capacity, total iron, and total aluminum. Given these factors and the fact that Ordnance Reef sediment samples were collected offshore, and many of these areas are under the influence of terrestrial runoff, these sediments can contain particles richer in As than those of reworked beach sand.

The various EQGs are proposed with the purpose of preventing adverse effects on biota from elevated concentrations of contaminants. In light of this, it is important to remember that much of the As measured in the samples collected may not be bioavailable. The sample digestion methods employed in this research are much more efficient at extracting As from soils and sediments than most organisms, and only a fraction of the total arsenic will be bioavailable. Furthermore, As toxicity is highly dependent on speciation. According to Bhumbra and Keefer (1994), "...arsenic mobilization in nature depends on the sources of arsenic, arsenic speciation, interactions of arsenic with soils, sediments, and geological materials, and transformations and translocations by soil microbes and higher plants."

## 5 Conclusions

Soils and sediment samples were collected on O'ahu, Hawai'i, from a variety of environments with varying degrees of human impact. Samples were classified as originating from areas of forested (conservation), agricultural, urban, mixed land use, or beach sediment. Surface ( $\leq 25$  cm) concentrations of As in all soils and sediments were found to range from 0.278 to 740 ppm with an overall median concentration of 8.09 ppm. The median surface As concentrations by land use were beach (2.75 ppm) < urban (9.09 ppm) < forested (9.20 ppm) < mixed (19.6 ppm) < agriculture (21.8 ppm). The beach sands may have had the lowest median As concentration because of the lack of As

binding sites available on carbonate materials in comparison with the iron oxide-rich soils typical of Hawai‘i. Although the surface As values we measured in agricultural lands were far less than those measured by Cutler et al. (2013) (estimated median = 230 ppm), they were consistently higher than the other land uses possibly due to previous use of arsenical pesticides or more recent use of As-enriched fertilizers (superphosphate, triple superphosphate, or micronutrient fertilizers). Nevertheless, the absolute highest concentrations of As (i.e., >500 ppm) were observed in forested areas, albeit either on or in the vicinity of flower farms.

The median surface As concentrations measured in this research (median = 8.09 ppm) were generally higher than median As concentrations previously measured in streambed sediments from O‘ahu, Hawai‘i (6.1 ppm, De Carlo et al. 2005), regardless of land use. Nevertheless, the median surface As concentrations measured for agricultural lands were nearly identical with 21.8 ppm for this investigation compared with 22 ppm for the NAWQA streambed sediments (De Carlo et al. 2005). The median As concentration in marine sediments collected as part of the Ordnance Reef Study (8.60 ppm, UHM 2013) was comparable to all but the highest concentrations measured during the 2007–2009 surface soil and beach sediment sampling. Moreover, the maximum As concentration from the marine sediments (43.9 ppm) was comparable to the maximum surface As concentration of 59.6 ppm, if the high values sampled along Waiakeakua Stream are excluded.

Our median As concentration for surface soils and sediments on O‘ahu of 8.09 ppm is higher than the geometric mean reported by Shacklette and Boerngen (1984) of 5.2 ppm. Because the geometric mean is an unbiased estimate of the median of lognormally distributed data (Helsel and Hirsch 2002), it is valid for us to compare the two values. Our median is also higher than the worldwide median As concentration of 5 ppm for soils reported by Riemann et al. (2009).

A total of 24 % of soil samples collected in this research exceed the HDOH soil EAL for As; 52 % of all soil samples exceed the CCME EQG for As in soils (12 ppm), but only 7 % (one sample) of all beach sands exceeded the NOAA marine sediment TEL for As of 7.24 ppm. On the other hand, 44 % of the marine sediments collected during the Ordnance Reef Study exceeded the NOAA marine sediment TEL. Interestingly, the latter were predominantly from the control area well away from the area of discarded military munitions. The exceedance of various criteria is not altogether surprising given that numerous authors cited above have reported that As is enriched in the marine environment although data from Hawai‘i do not entirely support that conclusion. Moreover, it is important to remember that arsenic toxicity is highly dependent on speciation and concentrations reported here are for total arsenic. Additionally, the digestion method used in this research allows dissolution of compounds that would not be bioavailable under normal environmental conditions.

Several questions remain outstanding following our most recent investigation into the distribution and abundance of arsenic (As) in the soils and sediments of O‘ahu, Hawai‘i. They are:

1. Why are the As values from samples collected along Waiakeakua Stream much higher (>500 ppm) than those measured elsewhere on O‘ahu?
2. Why are our As values from soils in former sugarcane lands on O‘ahu considerably lower than those measured by Cutler et al. (2013) in former sugarcane lands in the vicinity of Hilo on of the island of Hawai‘i?
3. Overall, even on O‘ahu, the median As concentration in soils was higher than the US or global medians. Why and what are the sources of this As?

4. Although the As concentrations we measured in marine sediments during the Ordnance Reef Study fall within the normal ranges for marine sediments, why do the concentrations vary so much across the various areas of that study and what As concentrations might we expect from the biota living in those areas?

If we use Reimann et al. (2009) as guide for future sampling, it is evident that considerably more samples will need to be collected with a higher spatial resolution. The good news is that based on our limited number of core samples, it will probably not be necessary to go much deeper than 50 cm, and in fact, it might be better to restrict our sampling to no more than 25 cm so we do not dilute our sample with lower As soils. We also need to compare the As data with other element data using an ordination technique such as principal component analysis or nonmetric multidimensional scaling in an effort to look for relationships between elements that might indicate less equivocally the source(s) of the As on O‘ahu. Moreover, it would be useful to collect soil data such as soil type, soil particle size distribution, and percentage organic carbon, and to collect information on past and current fertilizer use and past arsenical pesticide use.

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