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Arsenic accumulation by edible aquatic macrophytes

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ABSTRACT

Edible aquatic macrophytes grown in arsenic (As)-contaminated soil and sediment were investigated to determine the extent of As accumulation and potential risk to humans when consumed. *Nasturtium officinale* (watercress) and *Diplazium esculentum* (warabi) are two aquatic macrophytes grown and consumed in Hawaii. Neither has been assessed for potential to accumulate As when grown in As-contaminated soil. Some former sugarcane plantation soils in eastern Hawaii have been shown to have concentrations of total As over 500 mg kg^{-1}. It was hypothesized that both species will accumulate more As in contaminated soils than in non-contaminated soils. *N. officinale* and *D. esculentum* were collected in areas with and without As-contaminated soil and sediment. High soil As concentrations averaged 356 mg kg^{-1}, while low soil As concentrations were 0.75 mg kg^{-1}. Average *N. officinale* and *D. esculentum* total As concentrations were 0.572 mg kg^{-1} and 0.075 mg kg^{-1}, respectively, corresponding to hazard indices of 0.12 and 0.03 for adults. Unlike previous studies where watercress was grown in As-contaminated water, *N. officinale* did not show properties of a hyperaccumulator, yet plant concentrations in high As areas were more than double those in low As areas. There was a slight correlation between high total As in sediment and soil and total As concentrations in watercress leaves and stems, resulting in a plant uptake factor of 0.010, an order of magnitude higher than previous studies. *D. esculentum* did not show signs of accumulating As in the edible fiddleheads. Hawaii is unique in having volcanic ash soils with extremely high sorption characteristics of As and P that limit release into groundwater. This study presents a case where soils and sediments were significantly enriched in total As concentration, but the water As concentration was below detection limits.

1. Introduction

The accumulation of arsenic (As) from contaminated soils, sediments and water into edible plants presents a possible route for exposure to humans. Arsenic is a well-known human carcinogen affecting numerous organs, and As toxicity is associated with multisystem disease (Ratnaike, 2003). Exposure is usually from absorption through the small intestine, through ingestion of As in water, food or contaminated soil particles. Potential human health risks due to ingestion of plants containing As have recently received attention, especially for rice (Zhao et al., 2010). Additional studies documenting As uptake in vegetables, including vegetables irrigated with contaminated well water (Baig and Kazi, 2012) or grown on contaminated soil (McBride et al., 2013), and taro grown in contaminated soil and water (Kurosawa et al., 2008), further outline the possible risk of As through plant consumption.

The accumulation of As is also important in wetland species, where there is a potential for reducing conditions to release As into the soil solution (Ha et al., 2009; Rahman and Hasegawa, 2011), or for co-deposition of As with Fe hydroxides adsorbed to the plant's surface (Zhao et al., 2002). A wide range of aquatic macrophytes have commonly been used for their role in phytoremediation of organic and inorganic pollutants, including As, because of their capacity to accumulate metals in their tissues (Dhir et al., 2009; Rahman and Hasegawa, 2011).

There is a potential risk to human health due to consumption of contaminants accumulated by edible aquatic macrophytes, such as watercress and edible ferns. Robinson et al. (1995) found As levels of up to 500 mg kg^{-1} dry weight (DW) in the leaves of *Ceratophyllum demersum* (commonly called watercress), an aquatic, flowering plant found in a river system in New Zealand. Researchers were unable to conclude, however, whether the uptake was due to elevated concentrations of As in dissolved form in river water or in the sediments in which the watercress was grown. In a greenhouse experiment, they reported that watercress preferentially stores As in its leaves rather than in the stems (Robinson et al., 2003). Two reports have considered using the commonly

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eaten watercress species *Nasturtium officinale* for phytoremediation (Duman et al., 2009; Kara, 2002). The species accumulated Zn, Cu, Ni, Cd, Co, and Cr from contaminated wastewater.

A wide variety of ferns have been shown to accumulate As at high concentrations. The most widely studied accumulator is the Chinese brake fern (*Pterisvittata* L.), which has been shown to take up to 23,000 mg kg^{-1} of total As in its fronds (Ma et al., 2001). Other species of ferns have also shown high As uptake potential (Visoottiviseth et al., 2002; Zhao et al., 2002). Hawaii is unique in having a fern that is eaten as a delicacy. *Diplazium esculentum* (family Dryopteridaceae), the vegetable fern, known as warabi (from the Japanese), or ho'i'o or pohole (Hawaiian), is a woody fern that grows in wetland areas and along the banks of streams.

1.1. History of As contamination in Hawaii

In Hawaii, As-based herbicides, especially sodium arsenite, were used extensively at high application rates on sugarcane (*Saccharum* spp.) plantations for weed control in the Hilo, Hawai'i, area from 1913 to the 1950s (HDOH, 2007). Sodium arsenite was replaced by pentachlorophenol formulations followed by phenoxy and triazinine herbicides. Most sugarcane plantations in the islands had closed by the early 1990s. In recent years, new developments, including housing, schools and government buildings, seek to re-appropriate former sugar cane land for residential and commercial use, though some former sugar cane lands are also used for different types of agricultural practices (HDOH, 2009; Niemeyer, 2011). Arsenic contaminated soil continues to be found at levels up to two orders of magnitude above typical background levels of 1.0–20 mg kg^{-1} (Cutler et al., 2013).

The Hawaii Department of Health set an action level of 24 mg kg^{-1} for total As concentration in soil (HDOH, 2011). A similar limit does not currently exist for sediments. De Carlo et al. (2005) analyzed 24 sites on the island of Oahu, and found average sediment total As concentrations of 2.3, 8.1 and 22 mg kg^{-1} for forested, urban and agricultural sites, respectively. Although As has been found in extremely elevated levels in soils, As contamination of groundwater in Hawaii (as defined by the EPA maximum contaminant level of 10 μg L^{-1}) has not been documented by the Safe Water Drinking branch in many years of testing of public drinking water supplies (Cutler, 2011).

Previous studies of As in biota are sparse on Hawaii, and have focused on Waiakea Pond in Hilo, the site of a former Canec plant which manufactured bagasse-based insulation board treated with arsenic-containing compounds from 1932 to 1963 (Glendon-Baclig, 2007; Hallacher et al., 1985). The watercress species grown for consumption in Hawaii, *N. officinale* R. Br. (strain Sylvasprings) or the fern-species *D. esculentum* have not been tested for As.

In early 2011, exploratory soil samples were collected for As analysis at a site in Kaumana Springs Wilderness Area in Hilo, Hawaii. Extremely high As concentrations (up to 1000 mg kg^{-1}, measured by EDXRF) in surface soils were anecdotally reported in the adjacent field. The Kaumana Springs results were yet to be validated and extended, and the extent and severity of As risk in the Wilderness Area was unclear. The initial hypothesis was that As-laden sediments were being transported downslope from higher-elevation former sugarcane fields through erosion processes. Moreover, *N. officinale* is grown at the lower, easternmost, boundary of the Wilderness Area in the freshwater springs for community consumption. Given the low slope of lower KSW, redox potentials in wetland conditions may chemically release As from its bonds with Fe and Al-oxides.

It is hypothesized that aquatic macrophytes will accumulate As when in contact with high As soils. It remains unclear whether aquatic macrophytes grown for human consumption that come in contact with highly As-contaminated bank or field soils present a potential health risk to humans.

The objectives of this study were to (1) investigate reports of high As soil and determine the spatial extent and concentration of As in soil and sediments in Kaumana Springs Wilderness, (2) determine if aquatic macrophytes grown in a freshwater spring in contact with high-As soils and sediments accumulates As; and (3) assess risk to the community of exposure to As from consumption of *D. esculentum* and *N. officinale*.

2. Materials and methods

2.1. Site description

Kaumana Springs Wilderness Area (KSW) is 16 ha, located between the Wailuku and Waialua Rivers in eastern Hawaii at an elevation of 120–220 m (Fig. 1). The area receives 4250 mm of rain annually (Giambelluca et al., 2013). The soil is classified as Panaewa series, a ferrihydritic Lithic Hydrudand formed from volcanic ash over pahoehoe lava. The site has a complicated, not very well-documented hydrology that is categorized by lava tubes and dikes (Paquay et al., 2007). Two freshwater springs ("North" and "South") flow overland throughout the year. A third spring only surfaces at the lowest end of KSW, and is reported by local residents to connect to the "South" spring underground. The area has a slope of less than 2.5°, and the soil is often water saturated. Most of the area is used for cattle forage and is cordoned off by fences. At the lowest (easternmost) end of Kaumana Springs, there was evidence of depositional areas. Throughout the KSW, bank erosion was observed along the freshwater springs.

KSW supports small-scale *N. officinale* production at the lower (easternmost) end on the South branch of the springs. *D. esculentum*, which is often found near stream banks, was present in the same area. The local families reported that, to their knowledge, sugarcane had never been grown in the area and As-based herbicides had never been used (Sampaga, personal communication).

The first set of soil and sediments were collected in September 2011 at discrete points throughout KSW (sites A, B, C, and E), and resampled intensively at site D at the lower extent of Kaumana Springs (Fig. 1). The area referred to as lower Kaumana Springs, approximately 100 m by 100 m, was analyzed in four decision units (D-1, D-2, D-3, and D-4) that are progressively more downstream. A barbed-wire fence separated D-2 and D-3. A follow-up sampling took place in August 2012. *N. officinale* samples were collected at discrete sites D-1, D-2, D-3 and E, while *D. esculentum* was collected at site D-4. Freshwater samples were collected in August 2012 at site D-2. Duplicate water samples (1 L, in acid washed polyethelene containers, not filtered) of both the North and South stream were taken in August 2012.

2.2. Location of total As in KSW

In order to assess the spatial variability of site D, three experiments were designed. (1) The first study considered how total As varied with distance from the "North" branch of the freshwater spring. Samples were collected every 1 m from

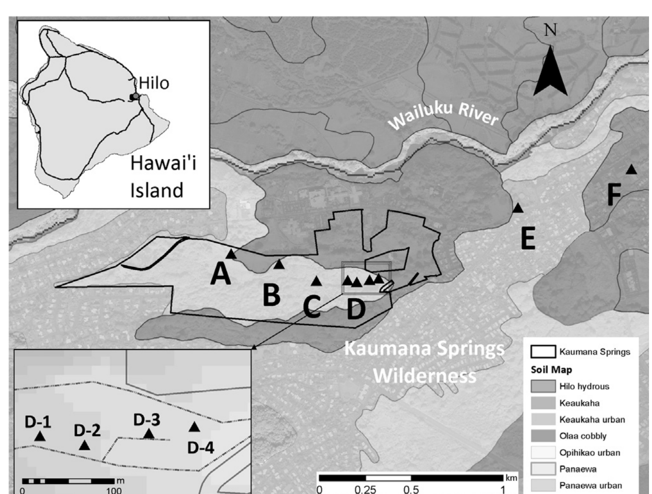

Fig. 1. Map of Kaumana Springs Wilderness and the surrounding area in Hilo, Hawaii. The elevation difference between the higher site A and lower site F is approximately 100 m. Freshwater springs flow on the north and south side of the Wilderness area, as indicated in the lower Kaumana Springs inset by the dashed line.