



## Iron amendments to reduce bioaccessible arsenic



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### HIGHLIGHTS

- Former sugarcane plantation soils contain elevated total and *in vitro* bioaccessible arsenic from historical herbicide application.
- Iron amendments effectively reduce arsenic bioaccessibility.
- Phosphate additions to iron treated and un-treated soils increase arsenic bioaccessibility.
- Iron amendments may be a cost-effective *in situ* remedy where the remedial objective is reduction of bioaccessible arsenic.

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### ABSTRACT

Former sugarcane lands on the Island of Hawaii have elevated levels of soil arsenic (As) from historical use of arsenical pesticides. The bioaccessible fraction of total As ( $As_{TOT}$ ), a measure of the potential for human As uptake by incidental ingestion of soil, is used in the assessment of human health risk and the determination of the need for remedial action. Ferric chloride plus lime and ferrous sulfate plus lime were applied to As-contaminated soils in a field plot setting to determine the potential for reducing *in vitro* bioaccessible As ( $As_{IVBA}$ ) by increasing As sequestration by the formation of additional iron (Fe) oxyhydroxides. The two Fe sources performed similarly in reducing  $As_{IVBA}$  over a 2-year observation period, with 30–41% reduction in  $As_{IVBA}$  for 0.25 wt% Fe dosing (dry soil basis) and 59–63% reduction for 0.5 wt% Fe dosing. Addition of phosphate ( $PO_4$ ) to treated and untreated soils caused a significant increase in  $As_{IVBA}$ . Iron-treated and control soils showed more than twice the  $As_{IVBA}$  after the addition of 1500 mg P kg<sup>-1</sup>. The cost of *in situ* treatment of As-contaminated soil with ferrous sulfate plus lime to lower  $As_{IVBA}$  was estimated to be an order of magnitude less than excavation and landfill disposal on the Island of Hawaii, making the technology a viable alternative when remedial action objectives were based on  $As_{IVBA}$  levels.

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## 1. Introduction

### 1.1. Problem definition, objectives

At many locations within the Hawaiian Islands, arsenic (As) has been identified in soils at concentrations significantly above

naturally occurring background levels [1]. Arsenic soil contamination is predominantly the result of historic spray application of inorganic As herbicides on sugarcane lands from 1913 to about 1950 [2], as well as release of As at herbicide storage and mixing areas. Extensive areas of former sugarcane cultivation on the Island of Hawaii show soil total As ( $As_{TOT}$ ) concentrations ranging from 40 to 900 mg kg<sup>-1</sup> [3]. The highest  $As_{TOT}$  concentrations, some greater than 20,000 mg kg<sup>-1</sup>, have been found at former pesticide mixing areas that were operated by various sugar plantations [4]. *In vitro* bioaccessible As ( $As_{IVBA}$ ), a surrogate for human oral relative bioavailability, ranges from less than 1% to more than 50% of  $As_{TOT}$  in Hawaiian soils [4]. The Hawaii Department of Health (HDOH) developed guidance for using the  $As_{IVBA}$  content of soil (not  $As_{TOT}$ )

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in assessing the potential for human health risk and determining the need for remedial action [5]. Soils with  $As_{IVBA}$  concentrations exceeding an action level of  $23 \text{ mg kg}^{-1}$  typically require some form of mitigation (remediation or controls) in an unrestricted land use setting.

Most agricultural soils on the Island of Hawaii are Andisols, young soils developed from the weathering of volcanic rock and tephra, rich in poorly crystalline to non-crystalline pedogenic solid phases, including iron (Fe) oxyhydroxides (ferrihydrite and goethite), aluminosilicates (allophane and imogolite), and metal–humus complexes [6]. The complexation of organic compounds to metals (Fe, Al) results in high total organic carbon content in Andisols [6]. Andisols display a strong affinity for inorganic As (arsenite/arsenate) and other oxyanions such as phosphate ( $PO_4$ ). Sequestering of As in these pedogenic solid-phase materials, in particular the Fe oxyhydroxide phases, is believed to be the dominant mechanism that results in low bioavailability and bioaccessibility of soil As [4]. The dominant controls on  $As_{IVBA}$  are the degree of As contaminant loading ( $As_{TOT}$ ) and the quantity of pedogenic substrate consisting of Fe oxides and oxyhydroxides, aluminosilicates and iron/aluminum (Fe/Al)–humus complexes. The concentration of pedogenic substrates can be estimated by citrate dithionite (CD) extractable Fe or Al [7]; or by total Fe ( $Fe_{TOT}$ ) content, which is positively correlated with CD-extractable Fe ( $Fe_{CD}$ ) [4].

Despite the strong natural capacity of Hawaiian Andisols to sequester As, some soils with high  $As_{IVBA}$  require remedial action. Traditional remedial technologies for As-contaminated soil consist of removal and landfill disposal, or capping, which can be costly and unsustainable due to limited clean soil sources. *In situ* treatment technologies to remediate soil by reducing  $As_{IVBA}$  may prove to be technically robust and cost effective at some As-contaminated sites.

### 1.2. Previous studies to reduce bioaccessible arsenic

Iron oxyhydroxides strongly sorb oxyanions of As, phosphorus, selenium, molybdenum and others [8]. Removal of dissolved As from wastewater using ferric iron compounds is a proven treatment technology [9]. The use of Fe-based soil amendments to reduce As mobility and toxicity has been extensively reported in the literature [10–12]. Sources of Fe have included agricultural or industrial grade chemical compounds (e.g., ferrous sulfate, ferric chloride), natural Fe oxide minerals and industrial waste by-products (e.g., fly ash, water treatment sludges, ore processing muds, Fe shot). Goals of soil treatment techniques have included reduction of As mobility (leaching), reduced uptake in crops, and reduced oral bioavailability to humans and ecological receptors. The following studies evaluated reduction of  $As_{IVBA}$  in response to Fe treatment.

Martin and Ruby [13] evaluated  $As_{IVBA}$  reduction (using the physiologically based extraction test [PBET]) [13] in lead- and As-contaminated soils from a smelter site by adding various soil amendments. They observed an 84% reduction in  $As_{IVBA}$  with the addition of 5 wt% ferrihydrite after a 33-week period of wet-dry cycling, and a 5-fold reduction in leachable As measured by the synthetic precipitation leaching procedure (SPLP; EPA Method 1312). Lombi et al. [14] showed approximately 25% reduction in  $As_{IVBA}$  in soils amended with Fe-rich wastewater treatment sludge. Mench et al. [15] determined that Fe grit reduced  $As_{IVBA}$  (PBET method) by 75% over a 6-year greenhouse study. Subacz et al. [16] evaluated efficacy of Fe amendments on As-contaminated soils amended in the laboratory with ferrous chloride, ferric chloride, ferric bromide and zerovalent (metallic) Fe, and found that over a 7-to-28 day testing period soluble Fe salts performed better at reducing  $As_{IVBA}$  than metallic Fe. On average,  $FeCl_3$  amendment at a dosing rate of 100 moles per mole As reduced  $As_{IVBA}$  by a factor of two; however, soil moisture content of at least 30% was required to facilitate

the observed reduction in bioaccessibility, and lime addition was necessary to control pH in soils lacking natural buffering capacity.

The current study builds on prior work showing that Fe amendments may provide significant reductions in  $As_{IVBA}$ . There is little information on the long-term viability of Fe amendments to reduce  $As_{IVBA}$  under field conditions. Our primary goal was to determine whether reduction in  $As_{IVBA}$  could be achieved and maintained over a period of several years in a garden plot setting using Fe-amendment products readily available in Hawaii (ferric chloride and ferrous sulfate). In addition, the reversibility of reduced  $As_{IVBA}$  by application of  $PO_4$  was explored, which could occur if  $PO_4$ -based fertilizers were applied to Fe-amended soils used for gardening, landscaping, or agricultural purposes.

## 2. Experimental

### 2.1. Study soils

The study site is located in the town of Kea'au, Island of Hawaii, on the east flank of the Mauna Loa volcano, and was formerly in sugarcane cultivation during the period of arsenical herbicide use. Study soils are Andisols (Great Group Hydrudands) formed from the weathering of underlying basaltic lava and subsequently deposited volcanic ash, at an elevation of 100 m above mean sea level with mean annual temperature of  $20.5^\circ\text{C}$  and annual rainfall of 4000 mm [17]. The age of the underlying lava is approximately 5000–11,000 y bp [18], above which a soil profile of approximately 1 m thick has developed. Andisols are characterized by andic properties in the fine soil fraction, including: low bulk density, high total organic carbon content, high  $PO_4$  retention, and significant ammonium oxalate-extractable (or citrate dithionite-extractable) Al and Fe [19]. The fine soil fraction (less than  $10 \mu\text{m}$ ) was examined by Cutler [4] using transmission electron microscopy (TEM). Three dominant pedogenic solid-phase materials were observed: Fe oxyhydroxides, short-range order aluminosilicates (allophane and imogolite), and metal–humus complexes. Less abundant phases included layered silicates (halloysite, smectite), opaline silica, and partially weathered volcanic glass. The test plot was located in Ap horizon soils (a former “plow” zone) with  $As_{TOT}$  content of  $790 \text{ mg kg}^{-1}$ .

### 2.2. Bioaccessible arsenic testing

*In vitro* bioaccessibility assays can be used to estimate relative oral bioavailability of metal(loid)s [13]. *In vitro* test methods used to evaluate bioaccessible As include the PBET, the *in vitro* gastrointestinal model (IVG) [20], and the method developed by the Solubility/Bioavailability Research Consortium (SBRC) [21,22]. These methods typically consist of a gastric phase extraction at low pH, followed by an intestinal phase extraction at near neutral pH. For this study we selected the gastric phase of the SBRC test (SBRC-g), which has been validated by Juhasz et al. [23] and Brattin et al. [24] with *in vivo* (swine) relative As oral bioavailability. The SBRC-g test consisted of extraction of 1 g of  $<0.25 \text{ mm}$  air-dried soil by 100 mL of glycine-buffered HCl (pH 1.5) at  $37^\circ\text{C}$  for 1 h. Filtered *in vitro* extract was analyzed for As and Fe by inductively coupled plasma (ICP) spectrometry. Quality assurance/quality control procedures included reagent blanks, reagent blank spikes, soil matrix spikes, duplicate sample analyses, and standard reference material (SRM) analyses [22]. Mean  $As_{IVBA}$  results for NIST 2710 SRM samples was consistent with (6% higher than) the value reported by Brattin et al. [24]. A second aliquot of soil was evaluated for  $As_{TOT}$  and  $Fe_{TOT}$  by acid digestion (EPA methods 3050B or 3051) and ICP analysis of the acid extract. HDOH provides guidance for contaminated soil assessment and mitigation based on  $As_{IVBA}$  expressed in concentration form [5]. The concentration of  $As_{IVBA}$  is the mass

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