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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⁻¹. 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

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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⁻¹ [3]. The highest As_{TOT} concentrations, some greater than 20,000 mg kg⁻¹, 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})

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 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°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 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°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

of As measured in the *in vitro* extract divided by the mass of the test soil. As_{IVBA} also may be expressed as a percentage by dividing the concentration-based form by the concentration of As_{TOT} (times 100).

2.3. Laboratory treatability testing

Laboratory treatability testing was conducted to determine Fe dosing rates for field trials. An Andisol with $580 \text{ mg kg}^{-1} As_{TOT}$ collected from the vicinity of the field test plot area was air dried and sieved to <2 mm grain size and amended with aqueous Fe solutions of ferric chloride ($FeCl_3$) and ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$). Soils were amended at dosing rates 0.25, 0.5 and 1 wt% on a dry soil weight basis. After adding Fe solutions, powdered hydrated lime ($Ca(OH)_2$) was added in stoichiometric proportion to Fe (1.5 moles lime per mole Fe) to prevent a drop in pH and promote ferric oxyhydroxide precipitation [16]. Soils were thoroughly mixed after lime addition, kept moist for 1 week, then air dried and sieved to <0.25 mm for As_{IVBA} analysis.

2.4. Field plot study

The field test plot consisted of 5 adjacent test cells, each $1.0 \text{ m} \times 0.5 \text{ m}$. Soils were tilled and stones greater than 2 cm in diameter were removed to a depth of 20 cm prior to placing cell dividers. Four cells were designated for $FeCl_3$ and $FeSO_4$ addition, each at two dosing rates, and a fifth cell was left un-amended as a control.

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

Soils from each cell were sampled prior to treatment and at 60, 135, 336, and 612 days post treatment. Sampling was performed using an incremental sampling technique [25] in which 50 randomly distributed sample increments of 5 g each were collected from the 0 to 20 cm depth interval and aggregated to create a master sample for analysis. Triplicate incremental samples were collected from each field plot during the final sampling event (612 d post treatment) for evaluation of sampling and analysis variance. Sampled soils were air dried and sieved to <0.25 mm prior to SBRC-g As_{IVBA} and As_{TOT} testing. Incremental subsampling was utilized to collect laboratory aliquots.

2.5. X-ray diffraction, transmission electron microscopy, targeted extractions, pH and redox measurements

Samples collected 336 d post treatment were evaluated by X-ray diffraction (XRD), transmission electron microscopy (TEM), reactive Fe content by the CD method [26,27] (with ICPMS analysis of the CD extract) and for pH and redox potential in 1:1 soil:water slurries. Poulton and Canfield [26] showed that the CD extraction provided the most complete dissolution of Fe oxyhydroxide and oxide pedogenic mineral phases, as compared to other common extraction techniques (e.g. hydroxylamine hydrochloride, ammonium oxalate).

2.6. Phosphate amendments of Fe-treated soils

For most soil-like materials, the sorption behaviors of PO_4 and arsenate (AsO_4) have been shown to be similar [8,28]. Phosphate has been shown to compete with As for sorption on Fe oxyhydroxides [29,30]. Violante and Pigna [31] evaluated the relative sorption of AsO_4 and PO_4 on selected phyllosilicates, metal oxides, synthetic organo-mineral complexes and soils. They determined that aluminosilicates (including allophane and non-crystalline Al hydroxide) and organo-mineral compounds sorbed PO_4 more strongly than AsO_4 . The opposite was observed for Fe, Mn, and Ti oxides and phyllosilicates rich in Fe, which were more effective at sorbing AsO_4 than PO_4 .

Soils collected 336 d after treatment were amended in the laboratory with PO_4 to evaluate reversibility of the lowered As_{IVBA} . Fifty gram subsamples of field-moist soils previously treated with 0.5 wt% Fe by $FeCl_3$ and $FeSO_4$, along with the control soil, were further amended with a potassium phosphate (KH_2PO_4) solution at dosing rates of 0, 240, 600, and 1500 mg P kg^{-1} soil (dry-weight equivalent) consistent with the range of potential PO_4 fertilizer additions in Hawaiian agricultural applications [32]. After PO_4 addition, soils were mixed and maintained at 23 °C and 80% humidity for two weeks, after which soils were air dried and sieved to <0.25 mm in preparation for SBRC-g testing.

2.7. X-ray adsorption spectroscopy

X-ray adsorption spectroscopy (XAS) was performed on 0.5 wt% $FeCl_3$ -amended and control soils collected 135 d post treatment, at beamline 10-ID (Materials Research Collaborative Access Team) at the Advanced Photon Source at Argonne National Laboratory, Argonne, Illinois, under parameters and conditions noted in [33].

Spectra were analyzed using the computer package IFEFFIT [34]. At least three spectra were averaged followed by subtraction of background through the pre-edge region using the Autobk algorithm [35]. The averaged spectra were normalized to an atomic absorption of one, and the EXAFS signal was extracted from the spectra. The data were converted from energy to photoelectron momentum (k -space) and weighted by k^3 . EXAFS spectra were calculated over a typical k -space range with a Hanning window and 1.0 width Gaussian wings. Fourier transforms (FT) were performed to obtain the radial distribution function (RDF) in R -space. Plotted R -space (\AA) data were not phase shift corrected; the true distances are between 0.3 and 0.5 \AA longer than the distances shown. The spectra were fitted with the FEFF8 computer code [36] which used *ab initio* calculations to determine phase shift and amplitude functions for single and multiple atomic scattering paths. Crystallographic structures for arsenate pentoxide (As_2O_5), scorodite ($FeAsO_4$), and alarsite ($AlAsO_4$) were used to develop theoretical fitting paths.

3. Results

3.1. Laboratory treatability testing

The soil utilized for treatability testing contained $580 \text{ mg kg}^{-1} As_{TOT}$ and $92 \text{ mg kg}^{-1} As_{IVBA}$. Reduction in As_{IVBA} was consistent with the magnitude of Fe-amendment dosing. For soils amended with $FeCl_3$ and lime, As_{IVBA} was reduced 18, 31, and 51% (*versus* control) for 0.25, 0.5, and 1 wt% Fe-equivalent dosing rates. Amendment with $FeSO_4$ and lime showed a similar trend of As_{IVBA} reduction with increasing amendment dosing; however, the magnitude of reduction was less than for $FeCl_3$. At the highest dosing rate of 1 wt% Fe-equivalent, a 22% reduction in As_{IVBA} (*versus* control) was observed, less than half of the reduction observed for $FeCl_3$ amendment at the same Fe dosing rate. The poorer performance of

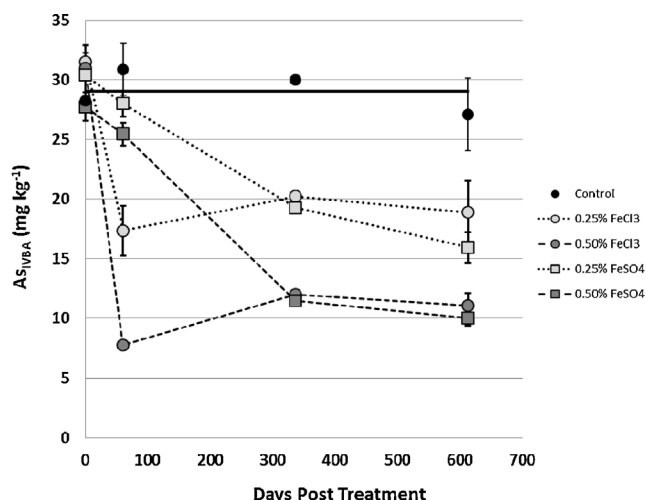


Fig. 1. Bioaccessible As in Fe-treated and control soils. Error bars for 0 day (pre-treatment) and 60 day samples show range of duplicate field incremental samples. Error bars for final (612 day) samples are ± 2 stdev of triplicate incremental samples. As_{IVBA} of control soil, shown as constant.

the $FeSO_4$ amendment may be due to the presence of SO_4 , which may compete with AsO_4 for adsorption on the newly formed Fe oxyhydroxide solid phases [37]. Based on bench-scale findings, both $FeCl_3$ and $FeSO_4$ were selected for field trials, at dosing rates of 0.25 and 0.5 wt% Fe to dry soil mass. The dosing rate of 1 wt% Fe was not carried forward to field trials, due to a high estimated cost for full-scale field implementation at this dosing level.

3.2. Field plot study

Basic properties of the field plot soils are provided in Table 1. Soils contained an average of $790 \text{ mg kg}^{-1} As_{TOT}$ and $30 \text{ mg kg}^{-1} As_{IVBA}$ (4% of As_{TOT}). Soils were slightly acidic (pH 5.6) and had total organic carbon (TOC) content of 11 wt%. Total iron content was 89.7 mg g^{-1} , of which 43 mg g^{-1} was reactive (CD-extractable). Fe_{IVBA} was 1450 mg kg^{-1} , representing 1.6% of Fe_{TOT} .

At 60 d post treatment, $FeCl_3$ -amended soils at 0.25 and 0.5 wt% Fe dosing rates showed 44% and 75% reductions in As_{IVBA} versus control (Table 2, Fig. 1). $FeSO_4$ -amended soils showed much less reduction in As_{IVBA} (9% and 18% reductions versus control, at the two dosing rates) at 60 d. Similar to observations from laboratory treatability tests, which were run for a 14 d period, the poorer performance of the $FeSO_4$ amendment after 60 d may be due to competitive adsorption between AsO_4 and SO_4 , which bind similarly to Fe oxyhydroxides (ferrihydrite) [38]. By 336 d post treatment, performances of $FeCl_3$ and $FeSO_4$ substrates in reducing As_{IVBA} were nearly identical, with 33–36% reduction in As_{IVBA} for 0.25 wt% Fe dosing and 60–62% reduction in As_{IVBA} for 0.5 wt% Fe dosing. Performance at 612 d post treatment was comparable with that after 336 d, with 30–41% reduction in As_{IVBA} for 0.25 wt% Fe dosing and 59–63% reduction for 0.5% Fe dosing. The apparent increase in As_{IVBA} for $FeCl_3$ -treated soils between 60 d and 336 d could possibly reflect a progressive increase in Fe oxyhydroxide crystal size [39,40] resulting in reduced As adsorption capacity.

Fe_{TOT} and Fe_{IVBA} in post-treatment soils were higher than in control soils due to Fe amendments. Fe_{TOT} concentration, as measured in the $<0.25 \text{ mm}$ soil fraction (used for IVBA testing) was significantly higher than the concentration of Fe added to bulk soil ($<2 \text{ cm}$ grain size) in the field test plot. Data clearly demonstrated an accumulation of Fe_{TOT} in the $<0.25 \text{ mm}$ (fine soil) fraction, 5–6 times greater than the bulk soil amendment dosing rate. Therefore, a given Fe dose applied to bulk soil has a magnifying effect on Fe

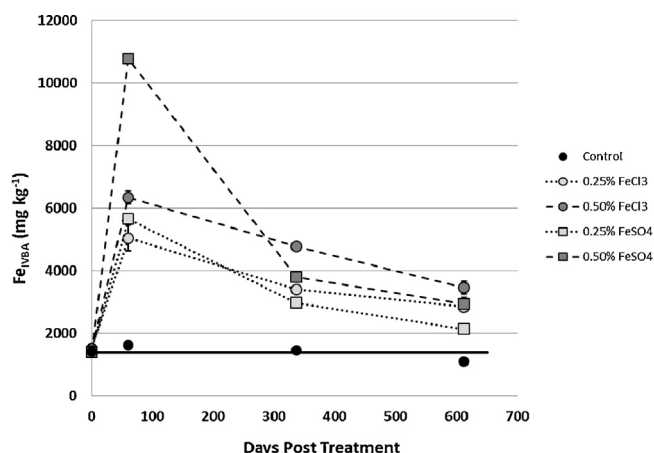


Fig. 2. Bioaccessible Fe in Fe-treated and control soils. Error bars for 0 day (pre-treatment) and 60 day samples show range of duplicate field incremental samples. Error bars for final (612 day) samples are ± 2 stdev of triplicate incremental samples. Fe_{IVBA} of control soil, shown as constant.

oxyhydroxide formation in the fine soil fraction used to measure bioaccessible As.

Fe_{IVBA} was 1450 mg kg^{-1} (or 1.6% of Fe_{TOT}) in pre-amendment soils and elevated in post-treatment soils (Table 2, Fig. 2). At 60 d post treatment, 4.9–8.8 wt% of Fe_{TOT} was extracted from Fe-amended soils by the SBRC-g test, as compared to 1.8 wt% from control soils. Soils amended with $FeSO_4$ showed higher Fe_{IVBA} than soils amended with $FeCl_3$. By 612 d post treatment, Fe_{IVBA} levels were below 3% of Fe_{TOT} for all treated soils.

3.3. X-ray absorption spectroscopy results

$FeCl_3$ -amended soil and control soils were collected 135 d post treatment and evaluated by X-ray Absorption Spectroscopy (XAS) to determine As speciation and As solid phase associations. X-ray adsorption near edge structure (XANES) spectra indicated that As was present in both soils as As(V), based on absorption maxima at about 11,875 eV (Fig. 3A). X-ray adsorption fine structure (XAFS) analysis indicated no difference in As speciation between $FeCl_3$ -treated and control soils (Fig. 3B). Structural parameters for the first shell (As–O) indicated a coordination number (CN) of 4 with an interatomic bond distance (R) of approximately 1.68 Å. The second shell for As–Fe scattering suggested a CN of 2 and R of 3.28–3.31 Å. These parameters point to arsenate speciation as bidentate binuclear complexes, consistent with arsenate ligand exchange sorption to Fe oxides and oxyhydroxides [41].

3.4. XRD, TEM, targeted extractions, pH and redox measurements

XRD and TEM were performed on Fe-treated and control soils from 336 d post treatment. In addition, the soils were evaluated for key soil properties including Fe_{CD} , pH, and (redox) potential. XRD showed no differences in crystalline phases, however TEM qualitatively indicated an increase in poorly-crystalline (ferrihydrite-like) materials in the Fe-treated soils. The pH of Fe-treated soils ranged from 6.3 to 7.0 versus 5.5 for control soils (Table 3). Redox potential of treated soils ranged from Eh of 482 mV to 528 mV, compared to the control soil Eh of 543 mV. Fe_{CD} ranged from 57 to 77 mg g^{-1} in treated soils, versus 43 mg g^{-1} in control soil. The redox and pH exhibited by Fe and lime treated soils were well within the stability range for ferric oxyhydroxide solid phase materials [42].

Table 1
Test plot soil properties.

Soil type	pH	TOC (wt%)	LOI (wt%)	As _{TOT} (mg kg ⁻¹)	As _{IVBA} (mg kg ⁻¹)	Fe _{TOT} (mg g ⁻¹)	Fe _{IVBA} (mg kg ⁻¹)	Fe _{CD} (mg g ⁻¹)
Hydrudands	5.6 ± 0.1	11.1 ± 0.1	33	790 ± 50	30 ± 3	89.7 ± 1.2	1450 ± 50	43 ± 0.5

<0.25 mm air-dried fraction; pH by 1:1 soil:water slurry; TOC = total organic carbon; LOI = loss on ignition at 750 °C; TOT = total element analysis by acid digestion and ICP; IVBA = *in vitro* bioaccessible fraction by SBRC gastric phase method, Fe_{CD} = "reactive" Fe by citrate–dithionite extraction and ICP. Uncertainties expressed are ± 1 st.dev. based on replicate analyses.

Table 2
Field plot–Fe amendment treatability study results.

Sampling event Dose	Total digestion			<i>In vitro</i> analysis				
	As _{TOT} (mg kg ⁻¹)	Fe _{TOT} (mg g ⁻¹)	ΔFe _{TOT} (mg g ⁻¹)	As _{IVBA} (mg kg ⁻¹)	As _{IVBA%} (% of As _{TOT})	ΔAs _{IVBA} (% Reduction)	Fe _{IVBA} (mg kg ⁻¹)	Fe _{IVBA%} (% of Fe _{TOT})
Pre-treatment								
Control	839	90.0	–	28	3.4	–	1420	1.6
0.50% FeCl ₃	772	89.7	–	31	4.0	–	1490	1.7
0.25% FeSO ₄	776	90.9	–	30	3.9	–	1420	1.6
0.50% FeSO ₄	783	89.0	–	28	3.5	–	1400	1.6
0.25% FeCl ₃	778	89.0	–	31	4.0	–	1500	1.7
60 days post treatment								
Control	872	90.8	–	31	3.5	–	1620	1.8
0.25% FeCl ₃	705	103	12.4	17	2.5	44	5040	4.9
0.50% FeCl ₃	730	128	36.9	8	1.1	75	6340	5.0
0.25% FeSO ₄	710	109	18.2	28	3.9	9	5650	5.2
0.50% FeSO ₄	648	122	31.4	25	3.9	18	10,800	8.8
336 days post treatment								
Control	854	88.6	–	30	3.5	–	1460	1.6
0.25% FeCl ₃	792	101	12.6	20	2.6	33	3400	3.4
0.50% FeCl ₃	793	121	32.6	12	1.5	60	4780	3.9
0.25% FeSO ₄	805	106	16.9	19	2.4	36	2980	2.8
0.50% FeSO ₄	756	117	28.7	11	1.5	62	3790	3.2
612 days post treatment								
Control	843	90.7	–	27	3.2	–	1090	1.2
0.25% FeCl ₃	775	99.9	9.2	19	2.4	30	2840	2.8
0.50% FeCl ₃	761	119	28.7	11	1.5	59	3460	2.9
0.25% FeSO ₄	794	104	13.6	16	2.0	41	2130	2.0
0.50% FeSO ₄	812	121	30.4	10	1.2	63	2930	2.4

Total and *in vitro* analysis on <0.25 mm air-dried soil fraction; ΔFe_{TOT} and ΔAs_{IVBA} are differences between treated and control soil for subject sampling event; coefficients of variance (CV) based on replicate analyses are: As_{TOT} 3%, Fe_{TOT} 1.3%, As_{IVBA} 5%, Fe_{IVBA} 2%.

Table 3
Soil properties, 336 days post treatment.

Dose ^a	Properties in <0.25 mm soil fraction							
	pH	Eh (mV)	Fe _{TOT} (mg g ⁻¹)	ΔFe _{TOT}		Fe _{CD} (mg g ⁻¹)	ΔFe _{CD}	
				(mg g ⁻¹)	(% increase)		(mg g ⁻¹)	(% increase)
Control	5.5	543	88.6	–	–	43	–	–
0.25% FeCl ₃	6.3	511	101	13	14	57	14	34
0.50% FeCl ₃	6.0	528	121	33	37	77	34	80
0.25% FeSO ₄	6.4	508	106	17	19	58	16	37
0.50% FeSO ₄	7.0	482	117	29	32	74	31	73

^a Dose is Fe addition to bulk soil, air dry weight equivalent, Ca(OH)₂ added at 1.5 moles/mole Fe; ΔFe_{TOT} and ΔFe_{CD} are differences between treated and control soil for subject sampling event.

Table 4
Phosphate amendment study results.

Dose P (mg kg ⁻¹)	As _{TOT} (mg kg ⁻¹)	As _{IVBA} (mg kg ⁻¹)	As _{IVBA%} (%)	ΔAs _{IVBA} (% increase)
Control soil–no Fe amendment				
0	697	28	4.0	–
240	731	38	5.2	34
600	716	46	6.4	65
1500	735	69	9.4	147
0.5% FeCl ₃ amended soil				
0	646	13	2.1	–
240	684	16	2.4	21
600	677	19	2.8	45
1500	653	28	4.4	114
0.5% FeSO ₄ amended soil				
0	666	12	1.8	–
240	699	16	2.3	31
600	695	19	2.7	54
1500	715	31	4.3	153

Dose P as KH₂PO₄ added to <2 mm soil fraction, air dry weight equivalent P, collected 336 d post Fe-treatment; As_{TOT}, As_{IVBA} measured in <0.25 mm soil fraction; ΔAs_{IVBA} is difference between P-amended and un-amended soil.

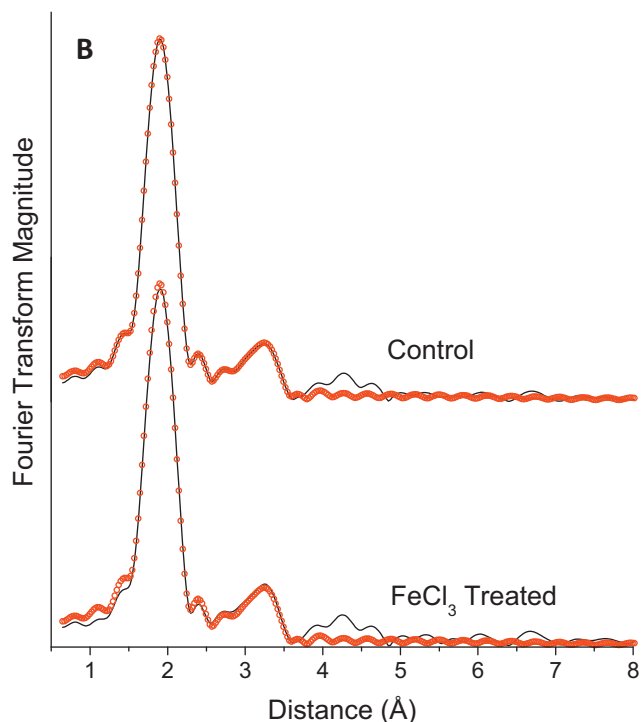
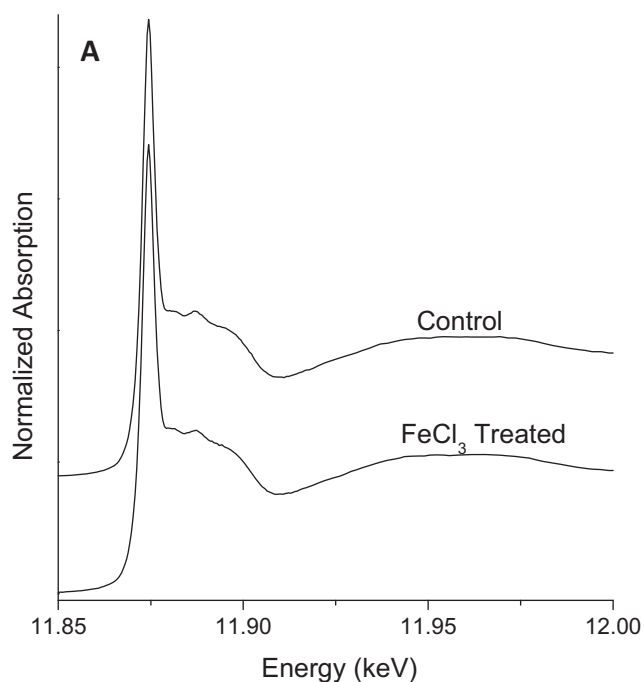


Fig. 3. Arsenic speciation determined by X-ray absorption spectroscopy. (A) X-ray absorption near-edge structure (XANES) spectra for the untreated control and the 0.5% FeCl_3 treated soil. (B) Extended X-ray absorption fine structure (EXAFS) Fourier transformed spectra of the untreated control and the 0.5% FeCl_3 treated soil. The black curve represents the sample data and open circles represent the calculated fit.

3.5. Phosphate amendments

Phosphate amendments caused substantial increase in As_{IVBA} measured two weeks after P addition (Table 4, Fig. 4). For control soils, the increase in As_{IVBA} was linearly proportional to the PO_4 dosing rate. Bioaccessible As measured 28 mg kg^{-1} with no PO_4 addition, and increased to 69 mg kg^{-1} at the maximum dosing rate of $1500 \text{ mg P kg}^{-1}$ soil, an increase of nearly 150%. For Fe-treated soils, the As_{IVBA} levels prior to PO_4 addition were 13

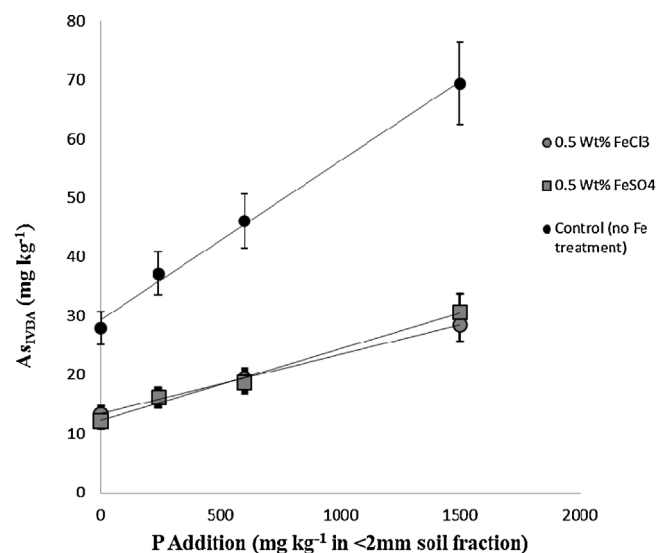


Fig. 4. Bioaccessible As in both control and Fe-treated soils shows linear increase after amendment with phosphate.

and 12 mg kg^{-1} (for FeCl_3 and FeSO_4 substrates, respectively), and As_{IVBA} increased linearly with respect to PO_4 dosing levels. At the maximum PO_4 dose of $1500 \text{ mg P kg}^{-1}$ soil, As_{IVBA} increased to 28 and 31 mg kg^{-1} in FeCl_3 - and FeSO_4 -amended soils (to levels above the HDOH action level of 23 mg kg^{-1}), representing 114% and 153% increases in As_{IVBA} over soils with no PO_4 addition. These percentage increases in As_{IVBA} were comparable to the increase observed in control soil. Addition of PO_4 increased As_{IVBA} in both control and Fe-amended soils.

4. Discussion

4.1. Formation of Fe oxyhydroxides

Several lines of evidence indicated that Fe amendments in study soils would result in formation of supplemental Fe oxyhydroxides with increased As sorption capacity that would reduce As_{IVBA} . Control soils and Fe-treated soils were qualitatively inspected by TEM. Treated soils appeared to contain more fine-crystalline Fe phases with ferrihydrite-like morphology. The new Fe oxyhydroxide in Fe-amended soils was selectively dissolved by CD extraction, indicating it was likely composed of oxyhydroxides similar to naturally occurring pedogenic phases (ferrihydrite, goethite). Fe_{TOT} , Fe_{CD} and Fe_{IVBA} were analyzed in soils collected 336 d post treatment (Table 3). The Fe_{TOT} in soils treated with 0.25 and 0.5 wt% Fe increased by 13–17 and 29–33 mg g^{-1} , respectively, compared to control. The Fe_{CD} in these same soils, treated with 0.25 and 0.5 wt% Fe, increased by 14–16 and 31–34 mg g^{-1} , respectively, compared to control. These similar results indicate that virtually all of the Fe introduced into soils by FeCl_3 and FeSO_4 amendments was present in the “reactive” (CD-extractable) state, likely composed of oxyhydroxide solid phases that strongly sorb PO_4 and arsenite/arsenate.

Iron oxyhydroxides became progressively more recalcitrant over time, as measured by Fe dissolved by the *in vitro* extract (Fe_{IVBA}). Sixty days after treatment, a large fraction of the Fe added to soils remained soluble in the *in vitro* acid extract, especially for the FeSO_4 treated soil (Table 2, Fig. 2). By 336 d post treatment, Fe_{IVBA} levels in FeCl_3 and FeSO_4 -amended soils were nearly identical, and at the final sampling event (612 d) the Fe_{IVBA} levels were not statistically different (Student's *t*-test, $p < 0.05$). These data indicated that ferric oxyhydroxides became more recalcitrant over time, possibly due to a progressive increase in crystallization and

reduction in surface area of the ferric solid phase materials [39,40]. Reduction in As_{IVBA} over time may be a direct result of progressively more recalcitrant Fe oxyhydroxides.

4.2. Arsenic binding to Fe oxyhydroxides

XAFS analysis indicates AsO_4 bonding to Fe oxyhydroxides, in both control and Fe-treated soils, with no evidence of Fe arsenate mineral formation. In previous work with historically contaminated soils [4], As_{IVBA} was found to be inversely correlated with reactive Fe content, where soils with higher Fe_{CD} exhibited lower As_{IVBA} . This observation suggests that As_{IVBA} could be decreased by increasing the Fe oxyhydroxide content of the soil.

Several processes may be occurring over time to lower As_{IVBA} in Fe-treated soils. These include redistribution of AsO_4 from pre-existing to newly formed Fe oxyhydroxide solids, progressive crystallization of Fe oxyhydroxides to more recalcitrant forms, and an increase in occluded arsenate within Fe oxyhydroxides solid phases. Some previous studies [43,44] have shown that As added to soils becomes less bioaccessible over time; however Kumpiene et al. [45] showed that 10 years after Fe treatment, As was preferentially associated with poorly crystalline Fe oxyhydroxides, which do not inhibit As uptake to plants. We are not aware of any studies showing the long-term (multi-year) effects of Fe amendments on As_{IVBA} ; however, our 2-year field trials indicated that this technology may be a viable long-term remedy where As_{IVBA} reduction is required. Longer term field studies would provide further understanding of treatment viability.

4.3. Conditions potentially increasing bioaccessible arsenic

Two geochemical processes could lead to increased As_{IVBA} in Fe-treated and untreated soils: (1) dissolution of the Fe oxyhydroxide due to low pH or reductive solubilization under low O_2 conditions [46], and (2) competitive displacement of AsO_4 by PO_4 or other oxyanions (such as citrate and malate that are present in composts and animal manures) [47]. Ferric oxyhydroxide solid phases are stable at the observed pH and redox conditions for treated and untreated soils in this study. Natural or human-induced conditions are unlikely to drive these soils into pH/redox conditions where ferric oxides become unstable. Reducing environments can develop in soils under flooded conditions or in the presence of organics (in soils amended with compost or manure, or below cesspools or septic fields), resulting in reductive dissolution of ferric oxyhydroxides and the concurrent release of As or other sorbed species [48,49]. However, ferric oxyhydroxide dissolution is unlikely for the Hydruand soils of the study area. First, the soils are highly permeable and typically well drained, due to porous lava rock beneath approximately 1 m of soil accumulation. In addition, the high concentration of reactive Al (oxalate-extractable Al) in these volcanic ash-derived soils may have an inhibitory effect on Fe reduction, even in submerged conditions [6].

Although ferric iron reduction and associated release of sorbed As is unlikely to occur in study soils, it may be a plausible consequence of application of PO_4 fertilizers to Fe-treated soils (or untreated soils) by gardening, commercial agriculture, or landscaping practices. Applied PO_4 could result in increased As_{IVBA} , as shown in laboratory treatability tests of this study, and also could be a concern for lead immobilization strategies that utilize PO_4 amendments in soils co-contaminated with As [50]. It should be noted that in our treatability test we used dissolved PO_4 , resulting in high pore water (soil solution) concentrations of PO_4 . Typical agricultural fertilizers, such as rock phosphate, triple superphosphate, or ammonium phosphate, are likely to result in a more sustained release of PO_4 to the soil solution. The effect of different fertilizer compounds, at a range of application rates, on As_{IVBA} cannot

be inferred from our preliminary bench-scale treatability testing. Further work in this area of potential environmental hazard is warranted, especially in locations where former sugarcane lands are being used for private or commercial agriculture. We emphasize that PO_4 addition to As-contaminated soils has the potential to significantly increase As_{IVBA} , whether or not the soils have been Fe treated. In selecting a robust remedy for reduction of As_{IVBA} using Fe amendments, institutional controls to prevent PO_4 fertilizer application should be considered a component of the remedy.

4.4. Potential full-scale implementation

Full-scale implementation of Fe amendment soil treatment should be feasible using conventional construction and farming equipment, such as deep tillage to provide adequate mixing of chemical reagents. Based on efficacy of this treatment in our study, the technology is expected to reduce As_{IVBA} by 25–50%. Agricultural-grade $FeSO_4$ is the recommended Fe source, because of lower cost and ease of application, as compared to $FeCl_3$. Based on the current costs in Hawaii for labor, equipment, and chemicals ($FeSO_4$ and lime), full-scale soil treatment at 0.5 wt% Fe dosing is estimated to cost approximately \$10/m³ of treated soil. This compares favorably to the current non-hazardous landfill disposal cost on the Island of Hawaii of approximately \$100 (US)/m³. In addition to lower cost, an *in situ* Fe treatment remedy provides additional benefit by not consuming limited landfill space that is currently needed for municipal solid waste disposal purposes.

Fe amendments to reduce As_{IVBA} may be particularly useful in soils with low levels of naturally occurring Fe oxyhydroxides and higher percentages of As_{IVBA} . Soils with low pedogenic Fe content in Hawaii include very young soils (Histosols), certain subsoils with high lithic content, and carbonate-rich soils in coastal areas.

5. Conclusions

Former sugarcane lands on the Island of Hawaii contain elevated levels of As_{TOT} and As_{IVBA} . Human health risk from incidental ingestion of As-contaminated soil could be reduced at certain sites by soil amendments. Previous studies have shown that Fe amendments can reduce the leachability, bioavailability (plant uptake), and *in vitro* bioaccessibility of As in soil. Our laboratory and field studies demonstrate that reagent mixture of either $FeSO_4$ plus lime or $FeCl_3$ plus lime will effectively reduce As_{IVBA} in volcanic-derived Andisols of Hawaii. At a dosing rate of 0.5 wt% Fe per dry weight soil, As_{IVBA} was reduced in field plots by approximately 60% after nearly one year post treatment. $FeSO_4$ plus lime did not perform as well as $FeCl_3$ plus lime 60 d post treatment, but performed similarly at the 336 d sampling event. The delayed efficacy of $FeSO_4$ versus $FeCl_3$ is not fully understood, but may be due to short-term competition between SO_4 and AsO_4 for sorption on the newly formed Fe oxyhydroxides. Iron amendments are believed to result in the formation of additional reactive Fe oxyhydroxides in the soil, strongly sorbing As and preventing its release in the *in vitro* bioaccessibility test. TEM and targeted chemical dissolution (CD extraction) indicate that the introduced Fe is present as a reactive Fe oxyhydroxide solid phase. X-ray adsorption spectroscopy indicates that all As is in the oxidized state ($As[V]$), and bonding of As in both Fe-treated and control soils is consistent with ligand exchange sorption to Fe oxyhydroxides. Addition of dissolved PO_4 to both Fe-treated and control soils increases As_{IVBA} . Use of PO_4 fertilizers on As-contaminated lands may increase the human health risk from incidental ingestion of soil. Iron-amendment remedies to reduce As_{IVBA} in soil may be more cost effective than a traditional excavation and landfill disposal remedy and should be considered if the remedial goals are reduction of direct exposure risk. Based on our 2-year field trials,

this technology may be a viable long-term remedy where As_{IVBA} reduction is required.

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