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Arsenic and iron speciation and mobilization during phytostabilization of pyritic mine tailings

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Abstract

Particulate and dissolved metal(loid) release from mine tailings is of concern in (semi-) arid environments where tailings can remain barren of vegetation for decades and, therefore, become highly susceptible to dispersion by wind and water. Erosive weathering of metalliferous tailings can lead to arsenic contamination of adjacent ecosystems and increased risk to public health. Management via phytostabilization with the establishment of a vegetative cap using organic amendments to enhance plant growth has been employed to reduce both physical erosion and leaching. However, prior research suggests that addition of organic matter into the oxic weathering zone of sulfide tailings has the potential to promote the mobilization of arsenate. Therefore, the objective of the current work was to assess the impacts of phytostabilization on the molecular-scale mechanisms controlling arsenic speciation and lability. These impacts, which remain poorly understood, limit our ability to mitigate environmental and human health risks. Here we report on subsurface biogeochemical transformations of arsenic and iron from a three-year phytostabilization field study conducted at a Superfund site in Arizona, USA. Legacy pyritic tailings at this site contain up to 3 g kg⁻¹ arsenic originating from arsenopyrite that has undergone oxidation to form arsenate-ferrihydrite complexes in the top 1 m. Tailings were amended in the top 20 cm with 100, 150, or 200 g kg⁻¹ (300–600 T ha⁻¹) of composted organic matter and seeded with native halotolerant plant species. Treatments and an unamended control received irrigation of 360 ± 30 mm y⁻¹ in addition to 250 ± 160 mm y⁻¹ of precipitation. Cores to 1 m depth were collected annually for three years and sectioned into 20 cm increments for analysis by synchrotron iron and arsenic X-ray absorption spectroscopy (XAS) coupled with quantitative wet chemical and mass balance methods. Results revealed that > 80% of arsenic exists in ammonium oxalate-extractable and non-extractable phases, including dominantly ferrihydrite and jarosite. Arsenic release during arsenopyrite oxidation resulted in both downward translocation and As^(V)

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attenuation by stable Fe^(III)(oxyhydr)oxide and Fe^(III) (hydroxy)sulfate minerals over time, highlighting the need for sampling at multiple depths and time points for accurate interpretation of arsenic speciation, lability, and translocation in weathering profiles. Less than 1% of total arsenic was highly-labile, i.e. water-extractable, from all treatments, depths, and years, and more than 99% of arsenate released by arsenopyrite weathering was attenuated by association with secondary minerals. Although downward translocation of both arsenic and iron was detected during phytostabilization by temporal enrichment analysis, a similar trend was measured for the uncomposted control, indicating that organic amendment associated with phytostabilization practices did not significantly increase arsenic mobilization over non-amended controls.

Keywords

phytostabilization; arsenic speciation; iron (oxy)hydroxides; ferrihydrite; jarosite; field-scale; depth profile; XAS

1. INTRODUCTION

Sulfide-ore derived mine tailings commonly exhibit low macronutrient content (N, P, Mg, K, Ca), acidic pH, low water holding capacity, and high concentrations of hazardous metal(loid)s such as Cr, Mn, Cu, Zn, As and Pb (Boulet and Larocque, 1998; Jamieson et al., 2015; Krzaklewski and Pietrzykowski, 2002; Lindsay et al., 2015). Mine tailings are a poor medium for vegetation establishment and growth, which makes them highly susceptible to wind and water erosion that transports toxic metal(loid)s in particulate or dissolved form to the surrounding environment (Anawar et al., 2015; Howell and Craw, 2014; Li and Huang, 2015; Mendez and Maier, 2008a; Shu et al., 2005; Tordoff et al., 2000; Yu et al., 2017). Therefore, remediation strategies are needed that can diminish the off-site transport of geodust and waterborne particulate and dissolved contaminants. Stabilization of arsenic in these mining impacted environments is of particular concern because it is a toxic carcinogen (Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). A cost-competitive, long-term remediation solution ideally suited for remote locations is phytostabilization (Ali et al., 2013; Mendez and Maier, 2008a; Mendez and Maier, 2008b). Indicators of successful remediation via phytostabilization are establishment of a resilient self-sustaining vegetation cover with low above-ground metal(loid) phytoaccumulation and development of dominant plant growth promoting neutrophilic heterotrophic microbial communities (Gil-Loaiza et al., 2016; Henry et al., 2013; Mendez and Maier, 2008b; Valentin-Vargas et al., 2018).

Despite the apparent utility of phytostabilization for low-cost remediation of mine tailings, there remains a need for geochemical analysis of its long-term effects on element lability and mobility in the subsurface. Although some previous studies have investigated the impacts of organic amendments on mineral weathering of pyritic tailings (Brown et al., 2009; Clemente et al., 2012; Lottermoser et al., 2005; Santibañez et al., 2012; Zornoza et al., 2012), no prior studies have resolved subsurface changes in arsenic and iron speciation as a function of depth on multi-year timescales. Given that soluble organic matter has the capacity to promote mobilization of arsenic from iron mineral sorbents by reductive dissolution, sorbate complexation, and ligand exchange (Mladenov et al. 2015), it is

necessary to elucidate the molecular mechanisms of arsenic lability change in tailings media subjected phytostabilization under relevant environmental conditions. Immobilization of contaminants during phytostabilization is a function of the extent of weathering of the unamended tailings and the amendment applied. Whereas climate and tailings lithology control weathering rates, the weathering process itself occurs at the grain scale, where fluid filled pores, sometimes in close proximity to each other, may exhibit sharp gradients in chemical composition and concentration, thereby exerting thermodynamic control over solid phase stability. The transport and reactions that occur at this pore-scale are complicated by mineral saturation and competition for surface sorption sites. For example, the addition of high phosphate organic amendment (Clemente et al., 2012) can compete for oxyanion surface complexation sites with arsenic, resulting in increased arsenic lability.

Results of prior investigations of metal(loid) mobilization with phytostabilization are mixed. For example, among the long term (2 years) field studies investigating phytostabilization of oxidizing pyritic tailings under a semi-arid climate, the pH values of unamended surficial tailings ranged from as low as 3.8 in sulfide ore tailings (Lottermoser et al., 2005) to as high as 7.98 in oxide ore tailings (Santibañez et al., 2012). While organic amendments generally corresponded with an increase in pH of acidic mine tailings (Brown et al., 2009; Clemente et al., 2012; Zornoza et al., 2012), effects on metal lability were variable. Lottermoser et al. (2005) reported an increase in lability associated with phytoaccumulation and hydrological transport of arsenic and metals, and Clemente et al. (2012) observed increased lability of Mn, Zn, As, Cd, and Pb, attributed to surface site competition from increased phosphate activity in the compost amendment. Conversely, other studies reported a decrease in plant available and water-soluble Cd and Zn (Brown et al., 2009; Zornoza et al., 2012), and a decrease in water soluble Cu (Santibañez et al., 2012).

Oxidative weathering of sulfidic tailings in (semi-)arid climate leads to the formation of Fe^(III) secondary mineral sulfates and (oxyhydr)oxides via incongruent dissolution of primary sulfide minerals, dominantly pyrite (FeS₂) (Foster et al., 1998; Hayes et al., 2014; Moncur et al., 2005; Romero et al., 2007). Common to weathering under (semi-)arid conditions is the retention in the near-surface environment (top meter) of sulfate and acidity that would otherwise be leached to depth and surface waters in more humid systems (Hayes et al., 2014; Murray et al., 2014). Precipitation of sulfate minerals such as jarosite and schwertmannite provides structural sites and reactive interfaces for arsenic retention. Despite the potential for arsenic attenuation by secondary weathering products (Murciego et al., 2011), environmental conditions required for phytostabilization (e.g., organic matter addition, irrigation, and associated changes in microbial community composition) are expected to alter the naturally occurring biogeochemical processes, potentially leading to the release of arsenic from solids to solution (Bauer and Blodau, 2006; Mladenov et al. 2015; Smedley and Kinniburgh, 2002).

The present field study investigated the multi-year effects of compost amendment and the established vegetation cap using native halotolerant plant species on the subsurface geochemistry of (mostly) oxidized pyritic mine tailings during phytostabilization in a semi-arid climate. Sampling was conducted annually for four years to about 1 m at four depth increments. The objectives were to (1) identify the impact of phytostabilization on arsenic

and iron speciation, lability and subsurface transport and (2) determine whether a decrease in metal(loid) lability corresponds with incorporation of labile elements into neoformed solid phases or subsurface translocation over time. We hypothesized that, despite the addition of labile carbon and irrigation water, the unique environmental conditions that accompany mine-tailings diagenesis under semi-arid climate – i.e., wet-dry cycles, sulfate retention, formation of arsenic-reactive secondary minerals (Hammond et al., 2018; Hayes et al., 2014) – would inhibit the mobilization of arsenic into solution (relative to what has been observed for more humid environments), and thereby promote its retention in the upper portion of the tailings profile.

Ideally, mine waste remediation results in long-term stabilization of arsenic against mobilization (Bernardino et al., 2016; Marques et al., 2009; Mendez et al., 2007; Salt et al., 1995; Vangronsveld et al., 2009). We investigated a *direct planting* phytostabilization approach whereby growth of a vegetation cover was intended to provide physical stabilization against erosion with low above-ground arsenic phytoaccumulation (Solís-Dominguez et al., 2011). Here, we specifically assessed the subsurface geochemical responses to phytostabilization over a three-year period by combining molecular spectroscopy with wet chemistry methods. Synchrotron X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) were used to quantify changes in molecular speciation and mineral composition, whereas element mobility was measured by sequential extraction and chemical enrichment/depletion across the weathering profile.

2. MATERIALS & METHODS

2.1 Site Description

The Iron King Mine and Humboldt Smelter site (IKMHSS) in Dewey-Humboldt, AZ, USA was added to the National Priorities List in 2008 due to arsenic and lead contamination. Whereas Arizona state regulations set arsenic soil remediation levels at $133 \mu\text{mol kg}^{-1}$ (10 mg kg^{-1}) (AZ, 2007), arsenic concentrations at the IKMHSS tailings average 53 mmol kg^{-1} ($4,000 \text{ mg kg}^{-1}$) in the top 0.5 m depth (Root et al., 2015), far exceeding remediation limits. Plant nutrients and heterotrophic microbial communities are limited, such that the tailings lack any vegetative cover despite having been deposited over 50 years ago (Gil-Loaiza et al., 2016; Hayes et al., 2014; Root et al., 2015). These tailings present an immediate risk to nearby populations from exposure to arsenic via wind dispersion (Csavina et al., 2012; Hill, 2016; Ramirez-Andreotta et al., 2013a; Ramirez-Andreotta et al., 2013b; Stovern et al., 2014; Youn et al., 2016) and previously uninvestigated subsurface transport of arsenic that potentially threatens shallow groundwater at 9–15 m depth. Groundwater flows east from the mine tailings site toward the Agua Fria River, a tributary that feeds into the metropolitan Phoenix water reservoir.

The phytostabilization experiment initiated in the mine tailings at the IKMHSS site (EPA # AZ0000309013) has the overarching goal of investigating the long-term efficacy of vegetation cap establishment and toxic metal(loid) containment by a compost-assisted direct planting approach. Parent materials at $> 1.5 \text{ m}$ depth in the IKMHSS site are dominated by ferrous sulfides (*ca.* $2,100 \text{ mmol kg}^{-1} \text{ Fe}$; $3,100 \text{ mmol kg}^{-1} \text{ S}$) (Hayes et al., 2014; Root et al., 2015). Ore derived abundant pyrite and co-associated metal sulfides (e.g., arsenopyrite,

galena, sphalerite) oxidize in the presence of $O_{2(aq)}$ to release iron, arsenic, sulfate, and protons into pore waters, creating acid mine drainage (Eq. 1).

The dominant arsenic bearing parent mineral in the IKMHSS tailings is arsenopyrite. The near-surface tailings exhibit acidic pH (2.3) and high total arsenic concentration (*ca.* 41 mmol kg⁻¹) as a result of arsenopyrite oxidative weathering to form As-bearing jarosite and As-sorbed (oxyhydr)oxide minerals (Gil-Loaiza et al., 2016; Root et al., 2015).

Sulfide dissolution reactions at the IKMHSS are typically incongruent where oxidative weathering of pyrite and arsenopyrite leads first to the formation of poorly-crystalline (oxyhydr)oxides (e.g., ferrihydrite) followed by the formation of (hydroxy)sulfates (e.g. jarosite) above the redox boundary at *ca.* 30 cm depth. Arsenic released as As(V)O₄³⁻ tetrahedra is adsorbed to Fe(III) mineral surfaces in bidentate binuclear coordination (²C) with octahedral iron (Root et al., 2015). The high concentration of arsenic in the tailings is one of the primary health concerns at the site.

2.2 Field Experimental Setup

The field site and phytostabilization experiment design, initiated in 2010, have been previously described (Gil-Loaiza et al., 2016; Hayes et al., 2014; Root et al., 2015; Solís-Dominguez et al., 2012). Compost treated plots were amended with a one-time addition of dairy-manure green-waste compost from Arizona Dairy Compost LLC (Anthem, AZ). Six sprinkler-irrigated field treatments included 0% compost control without seed, 10% (228 t compost ha⁻¹) compost with seed, 20% (456 t ha⁻¹) compost without seed, and 20% compost with seed, where percent is on a mass basis, and refers to the compost added per unit total mass of the top 15 cm of mine tailings (Fig. S1). Irrigated control (0% compost) treatments were established in edge plots of the field experiment to avoid cross-contamination. Prior to direct planting, the compost was mechanically tilled into each treated plot to *ca.* 15 cm depth. Straw was scattered over the amended plots at a rate of 6 t ha⁻¹ and crimped 10 cm deep into the tailings to decrease compaction by irrigation, seed predation by birds, dispersion by wind, and water evaporation from the substrate. Treatments were randomly distributed and replicated in quadruplicate for a total of 24 field plots (9.6 m × 15 m) with bermed borders to *ca.* 50 cm in height to minimize cross contamination of treatments.

Native halotolerant plant species (seed source: Desert Nursery, Phoenix, AZ) were selected for seeded treatments based on the high biomass production and low above ground arsenic bioaccumulation (Solís-Dominguez et al., 2012) and added to seeded treatments at the following rates: *Festuca arizonica* (56 kg ha⁻¹), *Buchloe dactyloides* (90 kg ha⁻¹), *Acacia greggii* (1 kg ha⁻¹), *Prosopis juliflora* (0.15 kg ha⁻¹), *Cercocarpus montanus* (11 kg ha⁻¹), and *Atriplex lentiformis* (56 kg ha⁻¹). The 15% and 20% compost and seeded treatments received seed from all six species while the 10% compost seeded treatments received only *Buchloe dactyloides* and *Prosopis juliflora*, which were determined to be most successful for

biomass production in a previous greenhouse study (Solís-Dominguez et al., 2012). Large shrub and tree species (mesquite and acacia) seeds were soaked in water for 24 h and then planted by hand to a depth of 2.5 cm along seed lines that were 30.5 cm apart, alternating the two species. Seeds and straw were applied by hand at night to avoid losses due to high daytime winds. All field treatments and the control received irrigation of $360 \pm 30 \text{ mm y}^{-1}$ in addition to $250 \pm 160 \text{ mm y}^{-1}$ of natural precipitation.

2.3 Sample Collection and Processing

Tailings cores (2.54 cm diameter, up to 91.4 cm length) were collected annually from each of the 24 plots in May-July of 2010 (time zero, t_0) to 2013 (t_3) (Fig. S1). Plots were divided into six subsections, bisected longitudinally, and trisected along the short dimension. Cores were positioned in alternating locations, flagged each year to avoid resampling near the same location. Immediately following collection, cores were capped, labeled for orientation, sealed with vinyl tape, placed on dry ice, and transported to the laboratory where they were stored at -15°C until processing (Fig. S2). Cores were processed under anoxic conditions in a nitrogen filled glove bag (95% N_2 , 5% H_2), whereby they were sectioned into four segments starting from the surface (0-20 cm, 20-40 cm, 40-60 cm, and 60~90 cm depth). The deepest segment (60-90 cm depth) varied in length as a function of core sample compaction, total core lengths ranged from *ca.* 75 – 90 cm. Quartered sub-segments were homogenized, freeze dried, sieved using a 2 mm mesh, and stored at -15°C until further processing.

2.4 Collection and Preparation of Mineral References

Solid phase references were collected and synthesized for comparison to field samples. Natural arsenopyrite was sourced from Ontario, Canada (Root et al., 2015). References for $\text{As}^{(\text{III})}$ and $\text{As}^{(\text{V})}$ sorbed to ferrihydrite were prepared following published methods (Gao et al., 2013). The arsenic reagents $\text{NaAs}^{(\text{III})}\text{O}_2$ (99%) and $\text{Na}_2\text{HAS}^{(\text{V})}\text{O}_4 \cdot 7\text{H}_2\text{O}$ (98%), were purchased from Sigma-Aldrich Co. (St. Louis, MO). Arsenic solutions of 0.1 mM were prepared using Barnstead™ Nanopure™ water. In a 35 mL polyethylene centrifuge tube, 0.1 mM arsenic solution was added to a ferrihydrite suspension of 5.0 g L^{-1} . This suspension was then equilibrated on an end-over-end rotator at 7 rpm for 24 h. The final suspension was centrifuged and washed with nanopure water. Arsenate and arsenite adsorbed ferrihydrite samples were prepared by the same method except that the arsenite sample was flushed with N_2 gas, sealed, and wrapped in aluminum foil to prevent atmospheric exposure and photochemical oxidation. Natural iron reference minerals included: ankerite [$\text{Ca}(\text{Fe}^{(\text{II})}, \text{Mg})(\text{CO}_3)_2$] from Pulaski County, Arkansas, USA; chlorite [$(\text{Mg}, \text{Fe}^{(\text{II,III})})_3(\text{Si}, \text{Al})_4\text{O}_{10}$] purchased from Clay Minerals Repository; and pyrite purchased from Wards Scientific (Hayes et al., 2014). Synthetic iron references prepared according to previously published methods included ferrihydrite [$\text{Fe}^{(\text{III})}_2\text{O}_3 \cdot 0.5(\text{H}_2\text{O})$] (Burleson and Penn, 2006; Gao et al., 2013) and K-jarosite [$\text{KFe}^{(\text{III})}_3(\text{OH})_6(\text{SO}_4)_2$] (Burleson and Penn, 2006; Driscoll and Leinz, 2005; Gao et al., 2013). All reagents used were ACS grade or better. The identities of all references were confirmed by XRD.

2.5 Chemical Characterization of Tailings

Specific chemical extractions and digestions were performed on IKMHSS mine tailings using freshly prepared solutions (< 24 h) from ACS grade (or better) reagents. Elemental composition for solutions deriving from sequential extractions, microwave-assisted (CEM Corporation, MARS 6) aqua regia digestions, and microwave-assisted HF/HCl/HNO₃ digestions was measured by inductively coupled plasma-mass spectrometry (ICP-MS, Elan DRC-II, PerkinElmer, Inc., Waltham, MA, U.S.A.) following extraction/digestion, filtration (0.2 µm GHP Acrodisc® syringe filter) and dilution by 1% ultra-high purity (UHP, OmniTrace®) HNO₃. Filters were prewashed with 10 mL 0.1 M ultrahigh purity (UHP) HNO₃ followed by 10 mL of DI water (18.2 MΩ-cm Barnstead™ Nanopure™). The first 2 mL aliquot of filtrate was discarded. Sample means and standard deviations were determined for the field-scale quadruplicates. Field-scale variation, which was greatly in excess of analytical variation, was used to report uncertainty throughout.

2.5.1 Sequential Extraction—Metal(loid) lability was determined using a three-step sequential extraction procedure, targeting operationally-defined pools of arsenic species present in the tailings media (Dold, 2003; Keon et al., 2001). The sequential extraction (Table 1) employed a 1:100 solid to solution mass ratio with the following steps and target analytes: (1) DI water, 18.2 MΩ cm⁻¹, 25°C, unbuffered, 1 h, targeting soluble salts; (2) 1 M monosodium phosphate (NaH₂PO₄, 25°C, pH 5.0, 24 h) targeting arsenic adsorbed to ferric (oxyhydr)oxides and (hydroxy)sulfates through anion exchange with PO₄³⁻; and (3) 0.2 M acid ammonium oxalate (AO, 25°C, pH 3.0, 2 hours, dark wrapped in Al foil), targeting poorly-crystalline Al, Mn, and Fe (oxyhydr)oxides and occluded arsenic (this method has also been shown to dissolve some schwertmannite and jarosite (Dold, 2003) (Table 1).

Suspensions were reacted on a reciprocal shaker for each step, then subjected to centrifugation (42,000 RCF for 25 min), followed by aspiration of the supernatant solution. Samples were washed on a reciprocal shaker with DI water for 30 min following steps 2 (NaH₂PO₄) and 3 (AO), and this wash solution (following centrifugation) was quantitatively combined with the extractant solution. All supernatant solutions were filtered through a 0.2 µm GHP Acrodisc® syringe filter (Pall Corp., Port Washington, NY), a hydrophilic membrane ideal for aqueous sample filtration with low biomolecule binding (<< 1%), acidified to pH < 2 by UHP HNO₃, diluted by 1% UHP HNO₃ in DI water, and stored at 4 °C prior to analysis by ICP-MS. An exception to filtration was made for step 1 (nanopure H₂O) of the sequential extraction which was instead centrifuged at 37,000 RCF (17,000 RPM) for 3 min to sediment the > 125 nm diameter particle size range to enable consideration of the colloidal fraction mobilized by irrigation and precipitation in the field environment. Duplicate samples from each column depth were also subjected to microwave-assisted aqua regia digestion using 1 g freeze-dried tailings sieved to 2 mm and digested in an acid mixture of 25% UHP HCl and 75% UHP HNO₃ according to EPA Method 3051A (USEPA, 2007) for ICP-MS analysis. Tailings pH values were measured on fresh splits from sequential extraction step 1 (DI H₂O) supernatant (within 24 hours of extraction step completion) at 25°C with stirring using a pH meter (VWR, Symphony B40PCID) and probe (VWR, Ross) calibrated at 4.01, 7.00, and 10.01 with buffer solutions (Thermo Scientific, Orion) followed by a pH check of a pH 2.00 buffer solution (Fisher Chemical, Certified Grade) to assure measurement accuracy.

2.5.2 Analysis of Elemental Enrichment—Total elemental concentrations were measured using microwave-assisted HF/HCl/HNO₃ digestion. One gram of freeze-dried tailings previously sieved to 2 mm was suspended in an acid mixture of 16.7% HF, 41.7% HCl, and 41.7% HNO₃ (all acids UHP Aristar® Ultra). Digestions settled for 24 h at room temperature prior to pipetting a fraction from just below the surface for dilution. Certified reference material (CRM) standards and well characterized samples including NIST certified Montana Soil 2711 and Iron King Mine tailings samples previously analyzed by a commercial lab (Activation Labs, Ontario, CA), including a 180 cm depth sample used as unweathered parent material reference for enrichment/depletion analysis, were compared with the elemental contents calculated from the applied HF microwave-assisted digestion method used in this research for quality control. Measurements were within $\pm 10\%$ of the certified or outside lab measurements for arsenic and iron totals, verifying precision and accuracy in sample preparation and analysis. Average percent deviation from certified values for Ti was slightly higher (17%).

To quantify translocation in the IKMHSS tailings over the course of the three year period associated with the phytostabilization experiment, enrichment and depletion of arsenic and iron were calculated using a mass balance approach (Brimhall and Dietrich, 1987). Total elemental concentrations were determined by ICPMS following an HF/HCl/HNO₃ microwave assisted digestion procedure were determined for 0% compost control; 10% compost with seed; and 20% compost with seed for t_0 (time zero) and t_3 (after 3 years) with respect to depth. Initial attempts to utilize elements traditionally considered “immobile” over diagenetic and pedogenic time scales (i.e., Ti, Zr, Nb) were unsuccessful because of the high random variation in their solid phase concentrations, presumably as a result of successive tailings deposition events. Conversely, the Si profile, which was consistent across treatments and with depth, and which we assumed to remain relatively constant over the three year period of the study, provided a stable background against which to measure any redox or other organic matter induced mobilization of As and Fe during the experiment itself. The Si-based element mass transfer coefficient ($\tau_{Si,j}$, Eq. 2) indicates depletion (negative values) or enrichment (positive values) of element j (As or Fe) relative to parent material.

$$\tau_{Si,j} = \left[\frac{C_{j,w}}{C_{j,p}} \times \frac{C_{Si,p}}{C_{Si,w}} \right] - 1 \quad \text{Eq. (2)}$$

The terms $C_{j,w}$, $C_{j,p}$ and C_{Si} refer to the concentrations of element j (As, Fe or Si) in the weathering zone (w) and parent material (p), respectively. Parent material was defined as the unoxidized tailings sample collected from 180 cm depth that was previously characterized (Hayes et al., 2014; Root et al., 2015).

2.6 X-ray Absorption Spectroscopy

Bulk synchrotron X-ray absorption spectroscopy (XAS) was performed at the Stanford Synchrotron Radiation Lightsource (SSRL), Menlo Park, CA, USA. Arsenic XAS collected on beam line 11-2 using a LN₂-cooled double-crystal monochromator (Si[220] crystal, $\phi = 90^\circ$), detuned 40% to reject higher order harmonics, with a 100-pixel monolithic solid state germanium fluorescence detector (Canberra, France). Iron XAS spectra were collected on

beam line 4-3 using a Si[1 11] crystal monochromator ($\phi = 90^\circ$), fully tuned with a passivated implanted planar silicon (PIPS) detector. Vertical slits were set to 2 mm for all samples, horizontal slits were varied to optimize detector linearity and minimize deadtime. Sober slits and Z-1 filters decreased inelastic scatter from reaching the detector. Aluminum foil was used as an additional filter during arsenic XAS collection to minimize lower Z fluorescence from samples with high iron. Measurements were collected at 77 K using a LN₂ cryostat. Replicate spectra were compared to assure beam damage was not occurring. Energy calibration for arsenic K-edge and iron K-edge was by assigning the maximum of the first derivative of arsenic foil to 11,867 eV and iron to 7,112 eV. Samples were collected in fluorescence mode with 3-5 replicate scans. All XAS fluorescence measurement scans were dead-time corrected, detector channels with poor signal to noise ratios removed, and averaged using the SixPACK software package (Webb, 2005). Deglitching and normalization to the edge step were performed using the Athena software package (Ravel and Newville, 2005).

2.7 XAS Linear Combination Fits

The number of references used in linear combination fitting (LCF) was constrained by previously confirmed species and minerals present in the IKMHSS tailings (as determined by XRD and XAS) allowing up to five species to be fit to a given spectrum (Hayes et al., 2014; Root et al., 2015) following a thorough analysis using a database consisting of *ca.* 30 references. Arsenic LCFs were performed on normalized spectra over the range 11,850 – 11,900 eV where oxidation states of arsenic were fit by As^(V) and As^(III) adsorbed to ferrihydrite and arsenopyrite as models for As^(V), As^(III), and arsenic sulfide, respectively. Iron LCFs were performed on over the range $k = 2$ to 12. The fit total was unconstrained (i.e., not forced to unity) and energy shifts of < 1 eV were allowed. Although previous research sets the detection limit on X-ray absorption near edge structure (XANES) component fit to $> 5\%$ (O'Day et al., 2004), fits were allowed to include components of $\sim 1\%$ where they were shown to be present by XRD, while also improving the XANES fit. The statistical parameter reduced chi-square (Red. χ^2) was used to compare the relative goodness of fit for IKMHSS tailings samples. The error, reported as confidence level (cl), reports the 1 sigma uncertainty, corresponding to a 68% confidence level for a normally distributed Gaussian distribution (Ravel and Newville, 2005)

3. RESULTS

3.1 Iron and Arsenic Speciation

Iron XAS analysis revealed the presence of iron-phases ankerite, chlorite, pyrite, ferrihydrite, and jarosite (Fig. 1). Spectra and associated LCFs for k^3 -weighted iron K-edge extended X-ray absorption fine structure (EXAFS) for the entire depth profile sampled at t_0 and t_3 are presented for 20% compost & seed (CS) (Fig. 1) and 0% compost control (Fig. S3) with reference mineral spectra displayed for comparison. Normalized LCF percent component values are shown (Fig. 1, Fig. S3) and non-normalized LCF results are reported in Table 2. The k^3 -weighted iron EXAFS reveal a depth-dependent weathering gradient from sulfides and carbonates at depth to ferric (oxyhydr)oxides and (hydroxy)sulfates at the surface (Table 2). Accelerated pyrite weathering for the 20% CS treatment compared to the

0% control suggests that phytostabilization accelerates the natural weathering trajectory (Table 2). Ankerite is only present in measurable quantities at > 40 cm depth for the to and t₃ 20% CS treatment as well as the t₃ 0% control and only detected at < 40 cm depth in the to 0% control in the 25-35 cm depth increment (Table 2). Compared to ankerite, pyrite weathering is more gradual with persistence at the surface (0-20 cm) for the 0% control; however, no pyrite was detected at the surface (0-20 cm) for t₃ 20% CS (Table 2). Chlorite, an iron bearing phyllosilicate, was relatively stable against weathering over the course of this study and as such was found to be present in all sample depths for both the control and treatments (Table 2). Weathering of ankerite and pyrite in both the control and treatment correspond with initial precipitation of ferrihydrite followed by formation of jarosite, where the greatest fractions of jarosite are present in the most highly weathered surface samples (Table 2). A phytostabilization treatment effect on iron mineral weathering is equivocal because the sums of ferric solid phases (*i.e.*, ferrihydrite and jarosite) in the t₃ 0-20 cm depth range for the 0% control and 20% CS were 77% and 76% of the total iron, respectively, although the control exhibited a greater jarosite formation, an increase of 19.6% for the control and a smaller increase of 6.4% for 20% CS.

Consistent with the Fe EXAFS LCF analysis, LCF of As K- α XANES also reveal a sulfide weathering gradient from depth to the surface. Arsenic K-edge XANES measurements and LCFs for selected treatments are shown as (a) *time series* (across all four years for given depth and treatment) and (b-c) *depth series* (down core for to and t₃ of field experiment) (Fig. 2). The LCF results are reported in Table 3. While arsenite (As^{III}O₃³⁻) was included in the initial fit iterations, no As^(III) was detected in any samples and it was not included in the final fits. Only the 0% Compost 180 cm deep to sample closely resembled the parent material arsenopyrite (100% in LCF) (Table 3). All other samples in shallower (40-90 cm) depths from to to t₃ were fit with at least 25% arsenate, showing that oxidative weathering of the parent material had occurred to depths beyond 60 cm, even at the beginning of the experiment (Table 3). Spectral fits indicate that over the course of the three-year experiment, a progressive increase in arsenate (As^VO₄³⁻) occurs at the expense of arsenopyrite (Table 3). This trend of increasing fraction of arsenate species over the course of the experiment is shown by the difference in arsenate fraction between to and t₃ samples as calculated from LCF of As K- α XANES (Fig. 3). The change in fraction of arsenate is positive for the 0-60 cm depth for both the 0% control and 20% CS samples (Fig. 3, Table 3).

3.2 Arsenic and Iron Lability

Sequential extraction data reveal higher iron (Fig. 4, Table S1) and arsenic (Fig. 5, Table S2) lability in surficial relative to deeper tailings. The water extractable iron pool reveals a treatment effect whereby phytostabilization amendment of 20% compost corresponds to a decrease in the water-soluble iron pool in the 0-20 and 20-40 cm depth increments compared to the 0% control and 10% CS treatment (Fig. S4). The response of arsenic to phytostabilization in surficial tailings showed the opposite effect, whereby the water extractable arsenic pool showed an increase in the 20-40 cm depth increment for composted treatments compared to the control (Fig. S5). The concentration of phosphate exchangeable iron and arsenic pools appear relatively unaltered by treatment effects (Fig. S4, S5). For arsenic, the combined total of water extractable and phosphate exchangeable pools are <

25% of the total arsenic for all years, depths, and treatments (Table S2). The water and phosphate extractions dissolve < 4% of total iron for all years, depths, and treatments (Table S1).

Over the three-year experiment, arsenic associated with poorly crystalline (oxyhydr)oxides increased by *ca.* 20% in the mid-profile sections (20–40 and 40–60 cm) for all treatments (Figs. 5, 6). Interestingly, the maximum change in AO-extractable arsenic showed a shift to deeper (40–60 cm) depth for the higher (20%) relative to lower (0% and 10%) compost amendments. The fraction of arsenic that is AO-extractable varies from 7 to 70%, depending on treatment and depth (Fig. S6). The increase in AO-extractable arsenic in the 20–40 cm and 40–60 cm depth increments (Fig. 6) corresponds with a statistically significant decline in residual arsenic for the same treatments and depth ranges (Fig. S9).

Trends in arsenic and iron release from the sequential extractions were further investigated by calculating depth-weighted averages for the entire 0–90 cm core for the controls and treatments (Fig. 7). This analysis clearly reveals time-dependent increases in AO-extractable arsenic for all treatments and controls. In the IKMHSS tailings, AO-extractable arsenic has been previously identified dominantly as arsenic adsorbed to poorly crystalline (oxyhydr)oxides (Root et al., 2015). Time-dependent results make evident that this AO-extractable arsenic pool derives directly from the non-extractable pool, known to be arsenopyrite, which decreases during phytostabilization (Fig. 7). A corresponding increase in extractability with time was not observed for iron (Fig. 7).

3.3 Arsenic and Iron Translocation

Although the total Fe: As molar ratios do not exhibit clear depth or time dependent trends, and they generally remain between *ca.* 30–60, total concentrations for both arsenic and iron exhibit a slight increase at depth over time (Table S1–S3 and Fig. S7). To assess subsurface mobilization of iron and arsenic, enrichment (+ τ) and depletion (− τ) of both arsenic and iron, relative to parent material, were calculated for each time and treatment point from the HF/HNO₃/HCl digestion totals (Fig. S8). The changes in iron enrichment (− τ_{Fe}) between t_3 and t_0 for the 0% control, 10% CS, and 20% CS treatments shows no significant change at the surface (0–20 cm), slight decrease (− τ) for the control and increase (+ τ) CS samples at 20–40 cm, and an increase for the 60–90 cm depth increment for all treatments, suggesting migration of iron from shallow to deeper tailings (Fig. 8). Similarly-calculated, corresponding τ_{As} values were nearly unchanged for 0–20 and 20–40 for all treatments, negative for 20% CS and the control at 40–60 cm depth increment and positive for the control and 20% CS at 60–90 cm, consistent with a corresponding migration of arsenic from 0–60 cm depth to deeper tailings for the control and 20% CS (Fig. 8).

3.4 Tailings Acidification

A defining characteristic of the IKMHSS tailings depth profile is low pH at the surface and increasing pH with depth (Table 4). The 20% compost amendment exhibits a greater buffering capacity against progressively decreasing solution pH over the course of the experiment compared to the 0% control and the 10% CS treatment (Table 4). The 0% control exhibits the lowest surface pH and remains relatively stable around pH 2.7 for all four

sampling times (Table 4). While the composted treatments all exhibited higher surface pH initially following amendment, both the 10% CS and 20% compost showed a decrease in surface pH, and approached the pH of the 0% control pH at 0-20 cm at t_3 , indicating exhaustion of buffering capacity (Table 4). While the surface (0-20 cm) pH of the 20% CS treatment also decreases with time, it never dropped below 4, suggesting sustained buffering during the phytostabilization experiment (Table 4). Decreasing pH in the 20-40 cm depth increment for all treatments and control for all years is consistent with acid generation from oxidative weathering of sulfides. The control and all composted treatments exhibit stability at near-neutral pH for the 40-90 cm depth range for all years, indicating stable sulfides (limited oxidation) and that the redox gradient was not driven to deeper depths (Table 4). As mentioned previously, the water extractable iron pools decreased for tailings that received 20% compost addition (Fig. S4). Linear regression of water extractable iron against pH reveals that both compost addition and pH correlate with a decrease in water extractable iron (Fig. 9). In contrast, water soluble arsenic does not exhibit a significant pH dependence, although sequential extraction data reveals increased water extractability of arsenic with organic compost addition (Fig. 9, Fig. S10).

4. DISCUSSION

Release of geologically abundant arsenic from legacy mining sites worldwide poses immediate global health concerns due to the physiological toxicity of arsenic. Implementing effective long-term, low-maintenance methods for arsenic stabilization is complicated by dynamic microbial processes, pH variation, and redox fluctuations, which alter arsenic molecular speciation (Morin and Calas, 2006). Hence, measuring arsenic speciation and lability in field sites requires a multi-faceted approach that combines molecular and field scale methodologies (Brown et al., 2017; Jamieson et al., 2015).

Whereas the phytostabilization aim of establishing plant cover for effective dust control at the IKMHSS site was successful (Gil-Loaiza et al., 2018; Gil-Loaiza et al., 2016), the present work was designed to determine if amending with compost could potentially promote arsenic mobilization via ligand exchange at adsorbent mineral surfaces, and reductive dissolution of arsenic bearing Fe(III) minerals. Such mechanisms of arsenic transport are suggested by previous studies of subsurface arsenic mobilization in response to added OM and flooding (Mladenov et al., 2015; Polizzotto et al., 2008). We found no evidence to support enhanced mobilization of arsenic in the presence of composted organic matter, and we attribute this to the sequestration of released As(V) into reactive secondary phases through abiotic and biotic mechanisms.

4.1 Impact of Phytostabilization on Arsenic Lability

By combining sequential extractions, total digestions, and X-ray absorption spectroscopic analyses we observed that downward mobilization of arsenic and iron at the IKMHSS tailings was coupled to irrigation, as required for phytostabilization, but it was not accelerated by organic matter infusion. This inference derives from the similar translocation trends for control and composted treatments, where the common amendment was supplemental irrigation (Figs. 4–5). Arsenic and iron mobilization during phytostabilization

were quantified from enrichment/depletion (i.e., τ) trends of elements comparing t_3 to values for the 0% control, 10% CS, and 20% CS treatments (Fig. 8). Although previous research has shown that organic matter (OM) competes with arsenic for adsorption to iron oxides and enhances environmental mobility (Bauer and Blodau, 2006; Redman et al., 2002), this was not detected in the field site.

A companion year-long controlled greenhouse mesocosm study using the same IKMHSS mine tailings (Valentin-Vargas et al., 2018; Valentin-Vargas et al., 2014), showed (arseno)pyrite weathering, the bioavailability of iron and arsenic, and microbial community composition were strongly controlled by pH. That study showed that increasing proton concentration was associated with increasing pore water concentrations of labile metal(loids), and a similar relation was observed here (Fig. 9). Over the course of the present field experiment, loss of both arsenic and mobilization of iron was observed particularly in the surface (0-60 cm), whereas normalized concentrations in deepest tailings (60-90 cm) appeared less altered. This indicates that where arsenic and iron were translocated to greater depths it was due to lowering of pH in the near surface, as promoted by acid generating bacteria (AGB), but a significant enhancement due to organic amendments and plants (CS) was not observed. Pearson correlation coefficients (r) were computed to assess the significance of the depletion relationship between arsenic and iron (i.e., τ_{As} vs. τ_{Fe}) (Fig. 10). A two-tailed t-test indicated a positive correlation between τ_{Fe} and τ_{As} to be statistically significant at the 95% confidence level ($r = 0.583$, $n = 12$, $p = < 0.05$).

The observation that translocation of arsenic and iron occurred to similar extents in the composted treatments and the control does not necessarily imply the same processes are active in the presence and absence of added OM. This similar outcome could be the result of distinct hydro-biogeochemical processes. We postulate that arsenic mobilization in the control was driven by AGB processes that were less prevalent in the tailings amended with compost. Valentin-Vargas et al. (2018) found that arsenopyrite oxidizing genera, *Acidithiobacillus* and *Leptospirillum* (Corkhill and Vaughan, 2009), were present in unamended controls but absent in composted IKMHSS tailings following two years of the companion mesocosm study. Furthermore, a microbiological investigation of phytostabilization at the IKMHSS field sites showed that pH 4 represented a threshold change in community composition, with pH > 4 having abundant plant growth promoting bacteria (PGPB), such as *Pseudomonas*, *Arthrobacter*, *Devosia*, *Pylobacterium*, *Sinorhizobium*, and *Hyphomicrobium*, and minimal AGB, whereas at pH < 4, tailings were dominated by AGB such as Fe-oxidizing *Leptospirillum*, and Fe-reducers *Acidobacter* and *Acidiphilium* (Honeker et al., 2019). Hence, beyond the direct proton consumption capacity of the compost itself, the presence or absence of AGB or PGPB in the phytostabilized tailings may explain the buffering of pH to > 4 in the amendment with 20% compost and plants for all years at all depths, while the near surface (0-20 cm) control had a pH of < 4 for all time points (Table 4). The absence of plants on the unamended control plots are expected to deter PGPB activity and promote acid generating chemolithoautotrophy, whereas organic root exudates and plant litter encourage PGPB activity and suppress AGB (Gil-Loaiza et al., 2016). The amended plots showed a surface pH buffering out to two years, but the absence of plants and organic matter in the control favored Fe-cycling and S-oxidizing bacteria, which led to progressive acidification. A sustained low pH (<4) inhibits plant growth and

ferric (hydr)oxide stability, resulting in some degree of arsenate sorbent solubilization (Figs. 7 & 8). The increase in AO-extractable arsenic at 20-40 cm for all treatments (Fig. 5) and the relative enrichment of labile arsenic in the near surface 0-40 cm, % AO arsenic for t_0 vs t_3 (Fig. 6), reflect the response to irrigation whereby iron and arsenic move from the near-surface (0-20 cm) to deeper tailings, with an increase in the control treatment compared to treatments with added organic matter. Because the water-extractable and phosphate-exchangeable pools were mostly unchanged, this indicates a relative transformation of the arsenic species from the residual, least extractable pool, to arsenic sorbed to $\text{Fe}^{(\text{III})}$ (oxyhydr)oxides and (hydroxy)sulfates.

The direct influence of plant roots on arsenic speciation is also important to consider. We previously showed (Hammond et al., 2018) that whereas ferrihydrite-bound $\text{As}^{(\text{V})}$ species predominated in the initial bulk mine tailings, the rhizosphere speciation of arsenic was distinctly different. Root associated $\text{As}^{(\text{V})}$ was immobilized on the root epidermis bound to ferric sulfate precipitates and within root vacuoles as trivalent $\text{As}^{(\text{III})}$ -(SR)₃ tris-thiolate complexes. MolarFe to-As ratios of root epidermis tissue were two times higher than the 15% compost-amended bulk tailings. Rhizoplane-associated ferric sulfate phases that showed a high capacity to scavenge $\text{As}^{(\text{V})}$ were dissimilar from the bulk-tailings mineralogy as shown by XAS and XRD, indicating a root-surface mechanism for their formation and/or accumulation (Hammond et al., 2018). Hence, fine root production and turnover in the phytostabilized plots very likely influences the redistribution and retention of arsenic in the near surface tailings.

The species transformation from t_0 to t_3 indicating a relative increase in arsenic lability also suggests increased bioavailability of arsenic in the oxic zone (0-60 cm) for the control and below the composted zone for treatments (20-60 cm). The top 15 cm that received compost (and seeds) shows less increase in lability and bioavailability (Fig. 6). Enrichment of arsenic and iron below the oxic zone suggests attenuation of the mobilized elements below 60 cm by adsorption or precipitation. At 60-90 cm depth, iron is primarily in the residual pools (*ca.* 88-92% of total iron), generally as pyrite, ankerite, and chlorite with negligible change in lability from t_0 to t_3 (Table 2 and Fig. 4). Arsenic at the 60-90 cm depth increment was found to be partly oxidized (36-37%) with a very small component (<1%) as highly labile soluble salt, 9-15% as phosphate exchangeable $\text{As}^{(\text{V})}$, 9-19% as $\text{As}^{(\text{V})}$ occluded in poorly crystalline iron (oxyhydr)oxides, and 63-82% unextracted arsenic occluded crystalline $\text{Fe}^{(\text{III})}$ minerals (e.g. As-jarosite) and arsenopyrite (Table 3 and Fig 5). Like iron, changes in arsenic lability from t_0 to t_3 for the 60-90 cm depth increment were negligible. However, as reported in previous studies of mining impacted environments (Park et al., 2016), the observed increases of chemically resistant arsenic and iron pools in the enrichment zone (60-90 cm) indicates that mobilized arsenic undergoes adsorption to, or coprecipitation with, ferric minerals at depth. Sulfide-stable reducing conditions dominate at the 60-90 cm depth, which are suitable for un-weathered arsenopyrite stability (Craw et al., 2003; Root et al., 2015), precluding arsenic release from that dominant host in deep tailings. This is made evident by linear regression analysis of total residual arsenic for samples collected in t_0 - t_3 (Fig. S9). While a statistically significant linear trend of annual weathering of residual arsenic pools, previously identified as arsenic occluded in $\text{Fe}^{(\text{III})}$ minerals and arsenopyrite, was observed for samples collected at the 20-40 cm and 40-60 cm depth increments, the

residual arsenic concentrations at 0-20 cm depth and 60-90 cm depth remained stable. For surface depths, arsenic XANES analysis indicates that residual pools remain stable due to near complete oxidation of arsenopyrite at the onset of this investigation. However, stable arsenic concentrations in the residual pool at 60-90 cm depth indicate negligible weathering over the course of the three-year experiment of arsenopyrite below 60 cm depth.

4.2 Arsenic Attenuation during Pyrite Weathering

Arsenic speciation analysis by XAS LCF of unaltered IKMHSS tailings pit samples revealed partial oxidation of the initially deposited sulfides prior to irrigation and vegetation establishment; total arsenic in tailings as deep as 38-54 cm was 37% As^(V) (Root et al., 2015). During this field trial, arsenopyrite oxidative weathering continued in both the presence and absence of established vegetation in samples as deep as 40-60 cm (Fig. 3). Notably, it was observed by a combination of XAS and sequential extraction analysis that despite complete oxidation of arsenopyrite in surface (0-20 cm depth) tailings by the third year of phytostabilization, >80% of arsenic is attenuated in solid phases extractable by AO and in residual Fe^(III) (oxyhydr)oxide and Fe^(III) sulfate minerals (Fig. 2 and Fig. 5). Furthermore, for all treatments, depths, and years, highly labile water extractable arsenic pools remained <1% of all arsenic in the IKMHSS tailings (Table S2). Oxidative weathering was also observed for iron minerals during phytostabilization. The weathering trajectory of pyrite shows a clear progression of ferrihydrite formation followed by jarosite in agreement with previous analysis of unamended IKMHSS tailings (Hayes et al., 2014). It is well documented that arsenate has a strong affinity for Fe^(III) (oxyhydr)oxide (Dixit and Hering, 2003; Gimenez et al., 2007; Root et al., 2007; Waychunas et al., 2005) as well as Fe^(III) sulfate minerals (Asia et al., 2009; Burton et al., 2008 (Burton, 2009)). Results demonstrate natural attenuation of liberated As^(V) by ferric oxyhydroxides and sulfoxides (products of pyrite oxidative weathering) in the IKMHSS tailings subsurface; in agreement with previous field studies (El Adnani et al., 2016; Fukushima et al., 2003; Lee et al., 2005; Root et al., 2015).

Arsenic released from the weathering of arsenopyrite in surface tailings observed by arsenic XANES analysis corresponded to both a depletion of total arsenic and an increase in solid-phase As^(V) attenuation by ferrihydrite- and jarosite-type minerals via inner-sphere adsorption or coprecipitation, respectively in deeper tailings. This observation has significant implications for future field-scale experimental design as it highlights the need for sample analysis at multiple depth increments over multiple time points to accurately interpret spatiotemporal dynamics related to lability and mobility. For this reason, future monitoring of the enrichment zone (60-90 cm depth) at the IKMHSS field site is required to determine the capacity of deep tailings to attenuate liberated As^(V) from surficial tailings.

5. CONCLUSIONS

Findings reported here support our initial hypothesis that the environmental conditions associated with weathering of sulfidic tailings under semi-arid climate would limit the mobilization of arsenic through organic matter-mediated mechanisms of ligand exchange and reductive dissolution. The results show that subsurface mobilization of iron and arsenic were correlated and occurred to similar extents for both the phytostabilization treatments and

controls. Despite the complete oxidative weathering of arsenopyrite in surface tailings by the third year of the investigation, liberated As^(V) was mainly attenuated by Fe^(III) (oxyhydr)oxide and Fe^(III) sulfate minerals in the solid phase. The retention of arsenic in planted treatments includes root zone enrichments with novel speciation relative to unplanted controls. Less than 1% of total arsenic was observed in the highly labile water extractable pool for any treatment, depth, and year. Critical to the experimental design of future field-scale investigations on elemental lability and mobility was the finding that arsenopyrite weathering in surface tailings corresponded an accumulation of solid-phase As^(V) at greater depths, below the rooting zone. This highlights the need for sampling at multiple depths and time points to accurately interpret arsenic mobilization and fate during phytostabilization.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.

Iron K-edge XAS of 20% Compost & Seed (CS) treatment. Iron K-edge EXAFS and Fourier transforms (FT) are shown for IKMHSS tailings core samples collected from the same 20% CS plot at the initiation of the experiment (t_0) and after year 3 (t_3). Samples are composites from each of four depth increments sectioned from the cores (0-20, 20-40, 40-60, and 60-90 cm). Solid black lines are data; red dashed lines are linear combination best fits. The bar graph shows percent fits of reference components in the LCF results. Fit results are reported in Table 2. Reference compounds include: jarosite, ferrihydrite, pyrite, chlorite, and ankerite. For 0% control see Fig S3.

Fig. 2.

Arsenic K- α XANES data for a) surface time series (0-20 cm, t_0 - t_3) and b-c) depth sequence (0-20, 20-40, 40-60, and 60-90 cm) in IKMHSS tailings for the control (0%) and 20% compost and seed (20% CS) treatments. Solid blue lines are references; black lines are data; red dashed lines are linear combination best fits. Reference compounds: natural crystalline arsenopyrite (Root et al., 2015) and arsenate adsorbed to synthetic ferrihydrite (Gao et al., 2013). Fit results are reported in Table 3. See electronic version for color rendering.

Fig. 3.

Change in the percent composition of $\text{As}^{(\text{V})}$ from t_0 to t_3 determined by As XANES. Depth indicated is the mid-point of the homogenized core sub-sample. There was no analysis of the t_0 60-90 cm depth control. Error bars represent the propagation of error from the confidence level from LCFs (smaller than the symbol where they are not displayed). Shaded region indicates a decrease in the fraction of arsenate between t_0 and t_3 .

Fig. 4.

Fraction of iron solubilized during each step of the sequential extraction, displayed as both stacked percent (left) and concentration (right). Percent extractable is relative to aqua regia digestible totals reported in Table S1. t_0 - t_3 refer to the initiation of the experiment (t_0) and one-year increments thereafter (t_1 - t_3). Error bars denote standard deviation for quadruplicate field replicates ($n = 4$). Refer to the electronic version for color.

Fig. 5.

Fraction of arsenic solubilized during each step of the sequential extraction, displayed as both stacked percent (left) and concentration (right). Percent extractable is relative to aqua regia totals reported in Table S2. t_0 - t_3 refer to the initiation of the experiment (t_0) and one-year increments thereafter (t_1 - t_3). Error bars denote standard deviation for quadruplicate field replicates ($n = 4$). Refer to the electronic version for color.

Fig. 6.

The percent change between t_0 and t_3 of acid ammonium oxalate (% AO) extractable arsenic relative to total (aqua regia digestion) arsenic for each treatment: control (pink square), 10% compost & seed (CS, white diamond), 20% Compost (C, blue circle), and 20% CS (green triangle). Plotted depth (cm) is the mid-point of the homogenized core sub-sample. Shaded region indicates a negative change extractable arsenic from t_0 to t_3 . Please refer to the electronic version for color.

Fig. 7.

Depth-weighted mean percent-extractable As (left) and Fe (right) for the control (0%), 10% compost with seeds (10% CS), 20% compost (C), and 20% compost with seeds (20% CS) treatments for t_0 - t_3 , where t_0 refers to the initiation of the experiment, and t_1 to t_3 correspond to each subsequent year. Fractional pools of As and Fe solubilized during the sequential extractions are relative to total As and Fe reported in Table S7. Error bars denote standard deviation among quadruplicate field replicates ($n = 4$).

Fig. 8.

The change in enrichment (τ) values for arsenic (left) and iron (right) with depth from the beginning to the end of the experiment, t_0 to t_3 , for 0% control, 10% CS, and 20% CS treatments using Eq. (2). Error bars show standard deviation among quadruplicate field samples. Actual enrichment values for t_0 and t_3 are shown in Fig. S8.

Fig. 9.

Water extractable iron (left) and arsenic (right) as a function of pH. Data points represent the depth-weighted mean of all four years (t_0 - t_3) and all four depth increments. Listed percent refers to weight percent of compost added to the top 20 cm, C = compost, CS = compost + seed. X-axis error bars denote standard deviation for field-quadruplicate samples ($n = 4$), y-axis error bars are the propagated standard deviation for field-quadruplicate samples in each of four years ($n=16$). The statistical parameters R^2 and p-value indicate goodness of linear fit and statistical significance, respectively. * indicates statistical significance and the 95% confidence level ($p < 0.05$) for a two-tailed t-test ($\alpha = 0.05$, $n = 16$). For plots separated by treatment, see Fig S10. Refer to electronic version for color.

Figure 10.

Relative change in enrichment/depletion for arsenic (τ_{As}) and iron (τ_{Fe}) from t_0 to t_3 for field treatments. Samples are from all depths of the 0% control, 10% CS, and 20% CS treatments. Data points and error bars represent the average and the standard deviation of quadruplicate field samples, respectively ($n = 4$). The statistical parameters r and p represent the Pearson correlation coefficient and statistical significance of the correlation between τ_{As} and τ_{Fe} at the 95% confidence level, respectively. * indicates statistical significance ($p < 0.05$) for a two-tailed t-test ($\alpha = 0.05$, $n = 12$).

Table 1.

Sequential extraction steps for mine tailings samples.

Step	Extractant	Conc. (M)	Solid: Solution	Time, Temp.	Target Phase	Ref.
1	DI H ₂ O, Milli-Q water 18.2 MΩ cm ⁻¹	--	1:100	1h, 25°C	Soluble salts	Dold, 2003
2	Na ₂ H ₂ PO ₄ monosodium phospahte, pH 5	1.0	1:100	24 h, 25°C	Exchangeable and adsorbed ions	Keon et al., 2001
3	Acid ammonium oxalate, pH 3 dark	0.2	1:100	2h, 25°C	Poorly crystalline Al, Mn, and Fe (hydr)oxides	Dold, 2003; Keon et al., 2001

Table 2.

Linear combination fits for iron EXAFS. Iron K-edge k^3 -weighted EXAFS least-squares linear combination fits over the $k(\text{\AA}^{-1}) = 2-7$ of IKMHSS tailings samples reported as percent component fit and estimated error. Spectra are shown in Fig. 1 and Fig S3 for amended tailings (20% compost) and no compost control (0%), respectively at the initiation of the experiment (t_0) and after year three (t_3). Estimated error, or confidence level (cl), in parentheses, reports the 1 sigma uncertainty on the %fit component, corresponding to a 68% confidence level for a normal distribution.

	time	Depth (cm)	Jarosite	Ferrihydrite	Pyrite	Ankerite	Chlorite	Σ^a	red χ^2^b
<u>Control (no compost)</u>	t_0	0-20	34.7(2.0)	26.5(3.9)	29.3(1.3)	--	22.8(2.1)	113.3	0.537
		25-35 ^d	--	43.4(1.8)	44.1(1.2)	5.5(1.5)	15.9(1.8)	108.9	0.004
		38-54 ^d	--	5.0(1.9)	52.7(1.3)	14.2(1.6)	22.6(1.9)	94.4	0.005
		180 ^d	--	--	74.1(1.5)	17.5(2.4)	18.4(3.1)	110.0	0.022
<u>Amended (20% compost)</u>	t_3	0-20	41.1(1.8)	36.0(2.6)	4.8(1.2)	--	18.1(3.9)	100.0	0.495
		20-40	14.8(1.6)	51.2(3.3)	11.8(1.0)	--	20.1(1.8)	97.9	0.371
		40-60	--	14.4(3.3)	52.1(1.7)	11.7(2.4)	17.5(3.2)	95.7	0.869
		60-90	--	--	76.2(2.1)	12.3(3.1)	10.5(4.0)	99.1	1.435
	t_0	0-20	15.8(1.6)	42.3(3.1)	28.4(1.0)	--	22.0(1.7)	108.5	0.340
		20-40	1.4(1.7)	30.2(3.4)	37.6(1.1)	--	23.3(1.8)	92.5	0.395
		40-60	--	--	65.7(2.0)	12.7(3.0)	20.7(3.9)	99.1	1.360
		60-90	--	--	75.8(2.3)	16.7(3.5)	19.3(4.5)	111.8	1.841
<u>Amended (20% compost)</u>	t_3	0-20	35.4(1.5)	40.9(2.8)	--	--	16.0(1.6)	92.3	0.337
		20-40	--	36.3(3.1)	42.1(1.5)	--	18.8(2.5)	97.2	0.788
		40-60	--	--	77.3(2.1)	15.9(3.2)	14.1(4.2)	107.3	1.562
		60-90	--	--	89.4(1.9)	12.5(2.9)	5.5(37)	107.4	1.257

^a Σ is the sum of components not normalized to unity.

^bReduced chi squared (red χ^2) is the sum of error divided by the degrees of freedom in the fit and is reported as a statistical indicator for how well the final fit compares to the EXAFS $k(\text{\AA}^{-1}) = 2-12$ data.

^dSamples from unamended IKMHSS tailings collected at the field site in 2010 (Hayes et al., 2014; Root et al., 2015).

Table 3.Linear combination fits to arsenic K- α XANES data^a

Treatment	Year	Depth (cm)	FeAsS	As ^(V) _{ads-Fh}	Σ ^b	red. χ^2 ^c
<i>all years, 0-20 cm surface samples</i>						
0% Control	t ₀	0-20	15.9 (1.1)	86.4 (0.9)	102.3	0.0037
	t ₁		5.7 (1.2)	96.9 (1.0)	102.6	0.0049
	t ₂		1.9 (0.9)	99.2 (0.7)	101.1	0.0027
	t ₃		0.5 (0.0)	100 (0.0)	100.5	0.0030
20% compost + seeds	t ₀	0-20	8.0 (0.9)	93.5 (0.7)	101.5	0.0027
	t ₁		2.4 (0.0)	100 (0.0)	102.4	0.0052
	t ₂		1.4 (0.0)	100 (0.0)	101.4	0.0039
	t ₃		0.4 (0.9)	99.9 (0.8)	100.3	0.0030
<i>t₀ & t₃, 20 cm below surface</i>						
0% Control	t ₀ ^d	25-35	11.5 (1.2)	94.2 (1.0)	105.7	0.0045
		38-54	65.4 (0.8)	38.3 (0.7)	103.7	0.0022
		180	100 (0.0)	1.7 (0.0)	101.7	0.0015
	t ₃	20-40	7.8 (0.8)	96.5 (0.7)	104.3	0.0023
		40-60	39.2 (0.6)	63.5 (0.5)	102.7	0.0010
		60-90	74.0 (0.5)	28.6 (0.4)	102.6	0.0009
20% compost + seeds	t ₀	20-40	12.5 (0.7)	91.1 (0.6)	103.6	0.0016
		40-60	73.6 (0.5)	28.5 (0.4)	102.1	0.0007
		60-90	68.3 (0.7)	38.7 (0.6)	107.0	0.0014
	t ₃	20-40	10.5 (0.7)	93.0 (0.6)	103.5	0.0015
		40-60	56.0 (0.6)	47.0 (0.5)	103.0	0.0010
		60-90	66.9 (0.6)	36.0 (0.5)	102.9	0.0011

^aLeast-squares linear combination fit results for normalized arsenic K- α XANES spectra in Fig. 4. Fit range: 11,850-11,900 eV. Spectra from each year in the time series (t₀-t₃) are presented. Reference compounds: natural arsenopyrite (Root et al., 2015) and arsenate (As^V) adsorbed ferrihydrite (Gao et al., 2013). Results are not normalized and reported as percent fit and confidence level, %fit (*cl*). *cl* is 1 sigma uncertainty, corresponding to a 68% confidence level for a normally distributed Gaussian distribution.

^b Σ is the sum of fit components.

^cRed χ^2 is the reduced chi squared statistical indicator for how well the components fit the spectral data, which is the error divided by the degrees of freedom in the fit.

^dSample collected at t₀ from an unamended pit in IKMHSS tailings (Hayes et al., 2014; Root et al., 2015).

Table 4.

Tailings pH as a function of treatment and depth

Treatment	Depth (cm)	PH			
		t ₀	t ₁	t ₂	t ₃
0% Control	0-20	3.0 (0.4)	2.8 (0.1)	2.8 (0.1)	2.7 (0.1)
0% Control	20-40	6.1 (1.2)	4.2 (1.3)	4.6 (0.9)	4.4 (0.8)
0% Control	40-60	6.3 (1.1)	6.2 (1.1)	6.3 (1.1)	6.9 (0.3)
0% Control	60-90	7.0 (0.3)	7.0 (0.5)	7.1 (0.2)	7.0 (0.4)
10% CS	0-20	4.3 (0.4)	3.8 (0.7)	3.3 (0.6)	2.8 (0.2)
10% CS	20-40	5.2 (1.7)	4.6 (1.8)	4.3 (1.6)	4.1 (1.6)
10% CS	40-60	7.0 (0.5)	6.5 (0.4)	7.1 (0.2)	7.0 (0.2)
10% CS	60-90	7.4 (0.2)	7.2 (0.2)	7.2 (0.4)	7.4 (0.3)
20% C	0-20	4.7 (0.8)	5.4 (1.5)	3.8 (0.4)	3.3 (0.5)
20% C	20-40	5.9 (1.0)	6.1 (0.4)	5.0 (1.2)	3.5 (1.0)
20% C	40-60	6.8 (0.2)	6.9 (0.1)	6.8 (0.4)	7.0 (0.1)
20% C	60-90	6.8 (0.2)	7.1 (0.0)	7.1 (0.1)	7.2 (0.3)
20% CS	0-20	4.7 (0.5)	4.4 (0.7)	4.4 (0.5)	4.1 (0.7)
20% CS	20-40	5.9 (0.9)	5.4 (1.2)	5.3 (1.5)	4.0 (0.8)
20% CS	40-60	6.5 (0.5)	6.8 (0.3)	6.8 (0.7)	6.8 (0.4)
20% CS	60-90	7.3 (0.1)	6.9 (0.1)	6.8 (0.2)	7.0 (0.2)

pH measured after the first step (nanopure DI water) of the sequential extraction (solid:solution = 1:100 mass basis) reported for depth, year, and treatment for IKMHSS tailings. Standard deviation for n = 4 field replicates is reported in parentheses. Listed percent refers to weight percent of compost added to the middle 20 cm, C = compost, CS = compost + seed.