



Potassium jarosite seeding of soils decreases lead and arsenic bioaccessibility: A path toward concomitant remediation

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Soils are common sources of metal(loid) contaminant exposure globally. Lead (Pb) and arsenic (As) are of paramount concern due to detrimental neurological and carcinogenic health effects, respectively. Pb and/or As contaminated soils require remediation, typically leading to excavation, a costly and environmentally damaging practice of removing soil to a central location (e.g., hazardous landfill) that may not be a viable option in low-income countries. Chemical remediation techniques may allow for in situ conversion of soil contaminants to phases that are not easily mobilized upon ingestion; however, effective chemical remediation options are limited. Here, we have successfully tested a soil remediation technology using potted soils that relies on converting soil Pb and As into jarosite-group minerals, such as plumbojarosite (PLJ) and beudantite, possessing exceptionally low bioaccessibility [i.e., solubility at gastric pH conditions (pH 1.5 to 3)]. Across all experiments conducted, all new treatment methods successfully promoted PLJ and/or beudantite conversion, resulting in a proportional decrease in Pb and As bioaccessibility. Increasing temperature resulted in increased conversion to jarosite-group minerals, but addition of potassium (K) jarosite was most critical to Pb and As bioaccessibility decreases. Our methods of K-jarosite treatment yielded <10% Pb and As bioaccessibility compared to unamended soil values of approximately 70% and 60%, respectively. The proposed treatment is a rare dual remediation option that effectively treats soil Pb and As such that potential exposure is considerably reduced. Research presented here lays the foundation for ongoing field application.

lead | soil | remediation | arsenic | bioaccessibility

Globally, soils are major sources of human exposure to lead (Pb) and arsenic (As). With limited options for remediation (1, 2), soil Pb has the potential to cause widespread adverse health effects. Children ≤ 5 y of age are especially at risk as Pb exposure may lead to significant developmental and neurological ramifications, in-part facilitated by increased exposure from hand-to-mouth activity (3, 4). In the United States, the Environmental Protection Agency (EPA) has set a 400 mg Pb kg⁻¹ screening level for bare soil in play areas and 1,200 mg Pb kg⁻¹ for other residential soils (5); however, the US Center for Disease Control (CDC) asserts that no blood lead level is deemed safe (4), making reduction of Pb exposure by soil sources critical. Additionally, soil arsenic (As) contamination is commonly present with Pb due to legacy Pb arsenate pesticide applications, or in areas naturally high in As that then experience anthropogenic Pb inputs (e.g., Pb-based gasoline, smelter by-products, Pb-based paint, etc.) (6, 7). Exposure impacts from As, similar to Pb, may cause a range of adverse health effects, with carcinogenic effects being the most notable (8, 9). Soil As concentration guidelines are highly disparate in the United States, ranging from 0.039 to 40 mg As kg⁻¹ (10), and 60% of the total soil As concentration is expected to bioavailable (11), thus creating a significant need to develop strategies that reduce As solubility upon ingestion.

To combat exposures to metal(loid) contaminants, multiple in situ soil remediation options have been evaluated, with the primary goal of decreasing contaminant bioaccessibility (solubility at gastric conditions) and thus bioavailability (absorption into the body) (3, 12–14). During the past 20 y, phosphate-based methods that promote conversion of soil Pb species to low bioaccessibility phases (e.g., pyromorphite) have received significant attention. However, application of phosphate compounds (e.g., phosphoric acid, triple superphosphate, etc.) to soils may promote mobilization of arsenate via competitive sorption effects that facilitate increased As release upon ingestion (13, 15). Additionally, the efficacy of Pb remediation via phosphate-based treatments is variable and meaningful impacts on Pb bioaccessibility may require considerable time (3).

The conversion of soil Pb to plumbojarosite ($\text{Pb}^{2+}_{0.5}\text{Fe}^{3+}_3(\text{OH})_6(\text{SO}_4)_2$), produces a low solubility jarosite-group mineral that is exceedingly stable at gastric pH (~1.5 to 3) conditions. Initial research found that soil suspended in deionized (DI) water which received

Significance

Soils are major pathways of lead and arsenic exposure, with excavation often the only effective remediation option. Here, we developed an in situ remediation methodology that considerably reduces lead and arsenic solubility upon ingestion (i.e., bioaccessibility) to protect human health, concomitantly, in soils. Remediation is accomplished by converting existing lead and arsenic phases into iron-hydroxysulfate minerals (i.e., jarosite) that are exceedingly stable at acidic conditions, advantageously providing protection at stomach pH. Treatment persists after restoration to environmentally nominal pH conditions (~6 to 8). The proposed treatment is cost-effective, potentially saving millions of dollars per acre while dually providing treatment to areas where excavation is not feasible. Research presented here facilitates future field experiments actively in development at U.S. EPA.

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The authors declare no competing interest.

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a slow addition of ferric sulfate— H_2SO_4 solution at $\geq 95^\circ\text{C}$ promoted plumbojarosite (PLJ) formation (16), representing a modification of a standard PLJ synthesis method to be performed in the presence of Pb-contaminated soil (17, 18). We then expanded upon this work by using a similar jarosite-group mineral, potassium (K) jarosite, to promote formation of PLJ in soil suspensions at room temperature conditions (19). Results from both research efforts yielded Pb bioaccessibility and bioavailability reduction to $<10\%$ (16, 19). These reductions are unparalleled by other current remediation options (13, 20, 21); however, development of new techniques for typical soils (i.e., not in well-mixed water suspensions) are needed to provide a means for field scale remediation for Pb and to assess impacts on As. The use of K-jarosite as the foundation for Pb and/or As remediation is supported because both Pb and As, as arsenate, have the potential to participate in substitution reactions with jarosite-group minerals in model and natural systems (22–26). Additionally, the presence of K-jarosite may promote seeding effects for jarosite-group minerals by acting as a nucleation site and by increasing the rate of jarosite mineral formation (17, 27, 28).

Here, we have developed multiple K-jarosite treatments that we tested at realistic soil conditions 1) to evaluate the efficacy of K-jarosite seeding techniques on PLJ formation, 2) to determine the influence of soil temperature and K-jarosite seeding rate on soil PLJ conversion, and 3) to assess the potential for concurrent Pb and As bioaccessibility reduction following treatment. Determining efficacy of these treatments in laboratory-based potted soil experiments will facilitate field experiments, ultimately allowing for the field deployment of the proposed jarosite-based remediation to Pb and/or As contaminated soils. Results from this research effort provide a rare remediation option that is highly effective at simultaneously reducing Pb and As exposure from soils.

Methods

Preparation of K-jarosite and Soils. Synthesis of K-jarosite was performed according to the well-established method showcased in Baron and Palmer (29). In summary, 51.6 g ferric sulfate pentahydrate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$; Sigma Aldrich) was dissolved in 300 mL of DI water (18.2 M Ω). The resulting solution was heated via hotplate to approximately 95 to 100 $^\circ\text{C}$ (1 atm) while being continuously stirred. Potassium hydroxide (16.8 g) was then slowly added to the heated ferric sulfate solution. The resulting solution was covered and continuously stirred for 4 h with intermittent temperature monitoring occurring every 15 to 30 min. The resulting suspension was then allowed to settle at room temperature for approximately 30 min. Precipitated mineral was then washed three times with DI water, decanted of excess solution, frozen as a wet paste, and freeze-dried (FreeZone 4.5, Labconco). Approximately, 30 g of precipitate was produced and confirmed as K-jarosite via X-ray diffraction analysis (*SI Appendix, Fig. S1*).

Soil containing 2,393 mg Pb kg^{-1} and 369 mg As kg^{-1} originating from legacy Pb arsenate-based pesticide (HPb-HAs) and a residential soil containing 746 mg Pb kg^{-1} and 6 mg As kg^{-1} derived from historic zinc smelter deposition (MPb-LAs) were chosen for this study (*SI Appendix, Table S1*). Here and throughout, these soils will be referred to, respectively, as high Pb – high As and medium Pb – low As (HPb-HAs and MPb-LAs, respectively). The soils were dried at room temperature for 2 d and then sieved to the $<250\text{-}\mu\text{m}$ size fraction.

Jarosite Remediation of Soils in Potted Soil Environments. Both HPb-HAs and MPb-LAs were treated at various conditions conducive for jarosite mineral formation in the presence or absence of K-jarosite. Each treatment condition was given a dedicated vessel and sacrificed upon the end of the treatment. Initially, 30 g of soil was used for each treatment and placed in a glass vessel. Synthesized K-jarosite (1 g) was mixed into each soil and then brought to field capacity. One vessel for each soil was also prepped without K-jarosite. Each vessel was dedicated to a specific reaction temperature to promote PLJ formation, because heat is a primary requirement for jarosite-group mineral formation and has previously been reported as essential when promoting conversion of aqueous soil suspensions to

PLJ. (16) Here, we report a range of reaction temperatures (room temperature, 40, 50, and 60 $^\circ\text{C}$) that are well below the 95 $^\circ\text{C}$ typically needed for the laboratory synthesis of PLJ. Soils were heated to the target temperature using a stainless-steel heating probe (OMEGA). Then, 10 mL of 0.5 M ferric sulfate–0.05 M H_2SO_4 (trace metal grade, Sigma Aldrich) was applied to each soil, bringing each soil to saturated conditions. Soils were lightly mixed via a spatula, then allowed to react at the target temperature for approximately 16 h. Following reaction, treated soils were isolated via centrifugation (MegaFuge 16R Centrifuge; Thermo Fisher Scientific) and were washed three times with DI water. Soils were then frozen at -20°C , freeze-dried, and stored in a desiccator at ambient temperature until bioaccessibility (EPA Method 1340) (30) and X-ray absorption spectroscopy (XAS) analyses.

Evaluating the Effect of K-jarosite Seed Rate and Stability. In addition to evaluating temperature effects on jarosite mineral synthesis, we also evaluated the impact of K-jarosite seeding rate on HPb-HAs treated at either 40 or 60 $^\circ\text{C}$. K-jarosite seeding rates were evaluated based on percent weight of K-jarosite relative to the soil weight. K-jarosite application rates of 0.8, 1.7, and 3.3% weight (wt) were evaluated. Reaction temperatures were selected based on previous potted soil experiments where both 40 and 60 $^\circ\text{C}$ resulted in significant PLJ formation at a K-jarosite application rate of 0.8% wt. Treatments without K-jarosite seed were also evaluated. Last, we performed a preliminary examination of the long-term stability of PLJ phases formed. Replicate samples of HPb-HAs treated at 60 $^\circ\text{C}$ with K-jarosite (0.8% wt) were used. Treated soils were brought to saturation via DI water and adjusted to pH 4 or 9 (± 0.15) using potassium hydroxide (Fisher). Soils were monitored hourly for the first day of treatment, weekly for the first month, and then monthly until experiment completion (9 mo, total). Soils were covered in parafilm and maintained at saturation throughout the experiment. As performed for the earlier experiments, all K-jarosite seeding and stability samples were washed with DI water, frozen (-20°C), freeze-dried, and stored in a desiccator until further analyses.

Elemental Analysis and In Vitro Bioaccessibility Quantification. Following sample treatment and plumbojarosite mineral synthesis and lyophilization, each sample and mineral was acid-digested in 15 mL polypropylene DigiTubes via a Teflon[®] coated graphite block DigiPREP MS digester (SCP Science, Quebec, Canada). The block digester was preheated to 95 $^\circ\text{C}$ and monitored via reference probe in aqua regia (2 mL of concentrated nitric acid and 6 mL of hydrochloric acid). The nitric acid was concentrated trace metal grade (67 to 70%, w/w) and distilled in-house via duoPUR quartz sub-boiling distillation unit (Milestone, Sorisole, Italy). The hydrochloric acid portion of the aqua regia was concentrated trace metal grade (32 to 34% w/w Optima[™], Fisher Scientific Inc., Waltham, MA). Approximately 0.1 g of sample was transferred to each vessel along with 3 mL of aqua regia acid for complete saturation. Caps were loosely placed on top of each sample vessel to avoid pressurization while reducing sample loss. Quality control samples were added to verify Pb and As recovery capabilities associated with the combined acid and sample matrix. Commercially available certified standards were used for instrumental standards and spiking solutions (SCP Science, Quebec, Canada). A method blank was included in the batch to determine a baseline contaminant concentration for the vessels, acid, and laboratory area and tools used to perform the experiment. A spiked blank was included to determine percent recovery of analytes of interest and to assess bias and precision of the acid matrix. Similarly, a spike of the plumbojarosite mineral was included to assess the percent recovery of the associated matrix. Each sample was digested in duplicate to determine precision and bias in accordance with US EPA Method 3050b (31). A NIST standard reference material (2710a: Montana I Soil) was used as a method capability control to assess and compare the recovery of a tested, similar matrix. After a pre-digestion period of approximately 10 min, the samples were placed on the heated digester block for 30 min at 95 $^\circ\text{C}$. Following the digestion period, the sample rack was removed from the digester and allowed to cool for 30 min before diluting to 15 mL total volume with Type 1 ASTM DI water. DI water was filtered in-house through a Milli-Q[®] Q-POD[®] water purification system (MilliporeSigma, Burlington, MA). The samples were stored at 4 $^\circ\text{C}$ until analysis via iCAP RQ ICP-MS (Thermo Fisher Scientific, Waltham, MA).

Bioaccessibility of soil Pb and As was measured using EPA Method 1340, a validated in vitro bioaccessibility assay that has been used extensively (30, 32, 33). In short, 0.5 g of sample was extracted for 1 h with 50 mL of glycine (0.4 M) pH adjusted to 1.5 using HCl. The extraction was held at $37 \pm 2^\circ\text{C}$ in a

hybridization oven (Amrex Instruments, Inc.) while mixing at 30 rpm. Samples were filtered [0.45 μm polytetrafluoroethylene (PTFE) syringe filter], stored at 4 °C, and analyzed using ICP-MS via EPA Method 6020B within 7 d of extraction.

Lead and Arsenic X-ray Absorption Spectroscopy. Soils pre- and post-treatment were investigated using bulk L_{III} -edge Pb and As K-edge X-ray absorption spectroscopy (XAS). Spectra were collected using the Advance Photon Source (Argonne National Laboratory; Lemont, Chicago) at beamlines 10-ID and 10-BM [Materials Research Collaborative Access Team (MRCAT)] (34). Approximately, 40 mg of sample were mixed with approximately 20 mg of boron nitride and made into a 7-mm pellet using a KBr pellet press (International Crystal Laboratories). Pellets were encased with a single layer of Kapton tape. The sample pellet was then mounted at a 45° angle to the incidence beam at the Sector 10-ID and BM beamlines and prepared for fluorescence measurements. A Vortex or Lytle detector purged with pure argon gas was used for fluorescence detection. Pb foil and sodium arsenate reference standards were mounted in front of the reference ionization chamber at 10-ID and 10-BM, respectively, allowing for simultaneous sample and reference spectra collection per scan. Incidence, transmission, and reference ionization chambers were all purged with pure nitrogen gas. The beamline was prepared for Pb L_{III} edge fluorescence measurements by scanning incident X-ray energy using a cryogenically cooled silicon (Si) double-crystal (111) monochromator. All samples were scanned from –200 to 400 eV relative to the Pb L_{III} -edge (13,035 eV) and from –200 to 550 eV As K-edge (11,867 eV) using a step scan technique.

Collected XAS data were then calibrated to the Pb reference foil or sodium arsenate standard, averaged, merged, background subtracted, and normalized using the Demeter software package (35, 36). Reference spectra were collected from a Pb reference foil or a sodium arsenate standard concurrently with sample Pb and As fluorescence data and calibrated to 13,035 and 11,874 eV, respectively.

Reference calibrated sample scans were then averaged for each sample, followed by background subtraction and post-edge normalization using the Athena program of the Demeter software package. (36) After XAS data processing was completed, we performed linear combination fitting (LCF) to identify Pb or As phases present. LCF was performed in Athena (36) for the first derivative of the Pb X-ray absorption near-edge spectroscopy (XANES) region from 13,010 eV to 13,100 eV (35), X-ray absorption fine structure (EXAFS) was used to perform LCFs for As in soils with spectra being fit from 2 to 11 \AA^{-1} . A library of 24 Pb XAS standards was used to probe potential components present in each sample (*SI Appendix, Table S2*). Standards were sequentially removed based on statistical improvement of fit (R-factor). Components contributing less than ten percent were removed, followed by refitting with remaining components (37–39). The combination of standards resulting in the lowest R-factor results, signifying the statistically best fit for the data, for each sample was reported. Ancillary Fe^{57} Mossbauer spectroscopy analyses were also performed to confirm the presence of jarosite-group Fe phases (*SI Appendix*).

Results and Discussion

Successful Conversion of Soil Pb to Low Bioavailability Plumbojarosite. Here, we demonstrate the effective conversion of soil Pb to low bioavailability plumbojarosite (PLJ) minerals for two soils of unique geochemical characteristics (Fig. 1). HPb-HAs, a Pb arsenate pesticide–contaminated orchard soil (19, 40), and MPb-LAs, a zinc smelter–contaminated residential topsoil, were evaluated (*SI Appendix, Table S1*) to determine efficacy of treatment for different Pb sources and concentrations (2,393 and 746 mg Pb kg^{-1} , respectively). Across all experiments conducted,

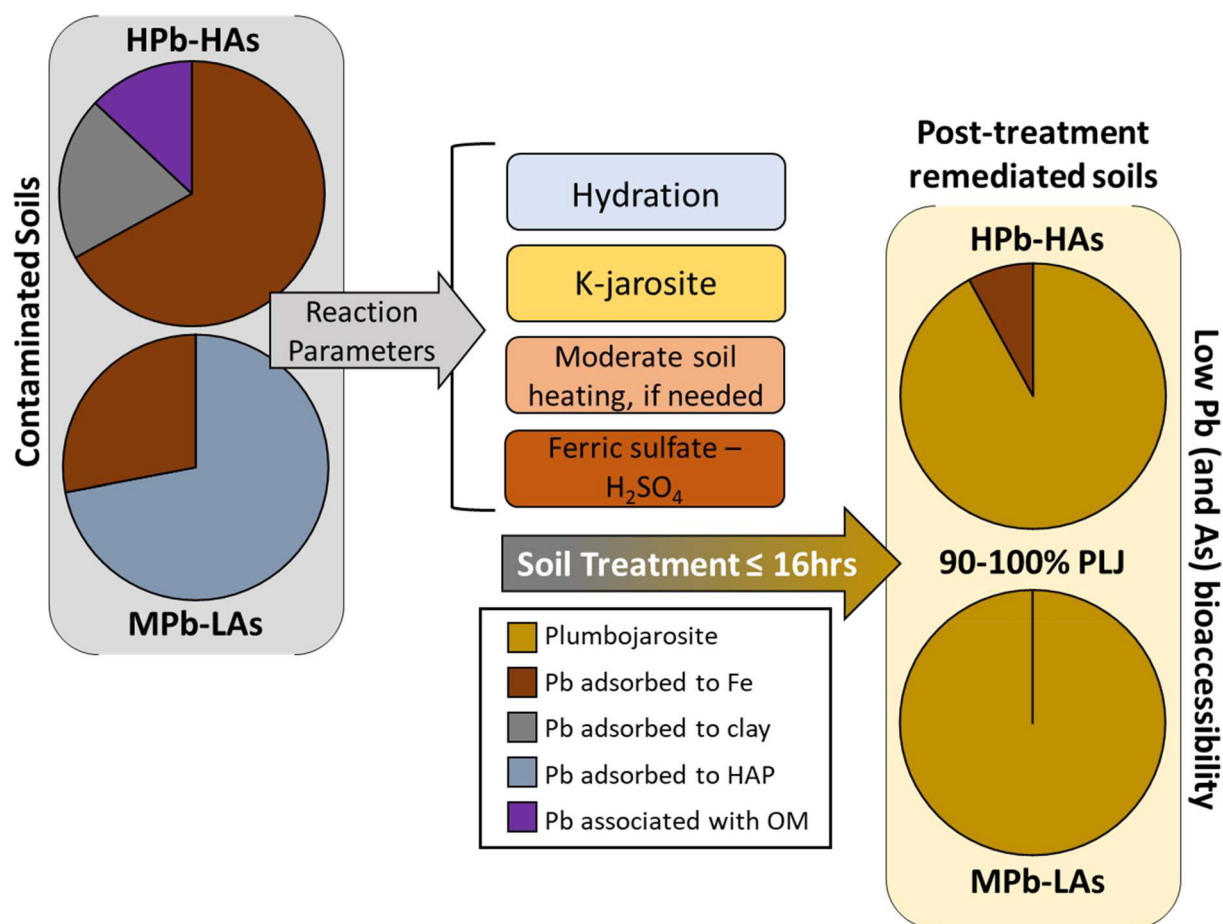


Fig. 1. Model showcasing two contaminated soils undergoing jarosite treatment in a potted soil environment. HPb-HAs represents a lead arsenate pesticide contaminated soil containing high [Pb] and [As] (2,393 mg Pb kg^{-1} and 369 mg As kg^{-1}), whereas MPb-LAs symbolizes a zinc smelter contaminated residential soil containing medium [Pb] and low [As] (746 mg Pb kg^{-1} and 6 mg As kg^{-1}). All treatments promoted a PLJ-conversion response. Pb speciation results correspond to Pb XANES LCF results (Fig. 2 and *SI Appendix, Table S3*).

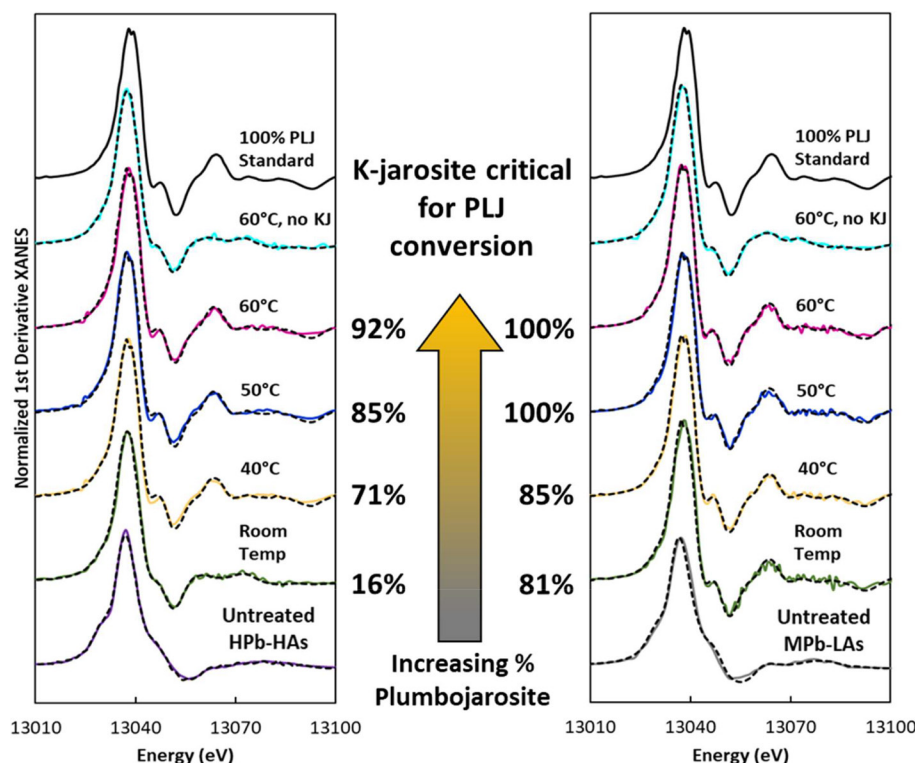


Fig. 2. Plumbojarosite (PLJ) conversion of soil Pb following K-jarosite treatment of HPb-HAs and MPb-LAs at different reaction temperatures and K-jarosite seed conditions. Both soils differ in initial Pb content and Pb source (*SI Appendix*). Potted soils were initially brought to saturation and allowed to dry over the reaction period (16 h) following K-jarosite treatment. Linear combination fitting of Pb X-ray absorption near-edge structure (XANES) spectra reveals PLJ percent of post-treatment soils. Tabulated LCF results and Pb and As in vitro bioaccessibility (IVBA) are provided in *SI Appendix*, Table S3. All standards used when performing LCF can be found in *SI Appendix*, Table S2 and spectra of standards are in *SI Appendix*, Fig. S2.

our treatment methods successfully promoted PLJ conversion, resulting in a proportional decrease in Pb bioaccessibility (*SI Appendix*, Tables S3 and S4). Specifically, we probed the conditions that influence maximum PLJ conversion and subsequent Pb bioaccessibility decrease.

We evaluated temperature conditions ranging from room temperature to 60 °C to assess the influence of temperature on PLJ formation (Fig. 2 and *SI Appendix*, Table S3). Successful conversion to PLJ was found at 40 °C for HPb-HAs (71 ± 3.2% PLJ) and room temperature (22 °C) for MPb-LAs (81 ± 2.1% PLJ). Increased soil temperature was found to be favorable to PLJ formation, especially for HPb-HAs, but PLJ formation beyond 71% is not necessarily needed for successful soil Pb remediation. Sequestration of 71% of the Pb as PLJ will considerably reduce the concentration available for solubilization upon ingestion, as Pb in PLJ is less than 1 percent bioavailable due to significant stability in acidic conditions (41). Therefore, while more PLJ formation may be observed at higher temperatures, increased formation may not be needed to meet remediation goals. A longer reaction period than 16 h may also facilitate continued PLJ conversion at room temperature, as increased temperature is expected to be driving the rapid kinetics of PLJ formation observed. Lastly, soil heating is achievable, especially to 40 °C, using a combination of soil heating probes, soil wrapping, and/or soil steaming. Specifically, economical solutions such as covering soils with a plastic sheet in summer months may generate sufficient heat to treat highly contaminated soils requiring minimal heating for effective treatment. However, specific methods of field application parameters will be evaluated in future field-testing efforts.

Concentration of Pb in each soil is expected to be a major factor driving the increased temperature needed to treat HPb-HAs compared to MPb-LAs. HPb-HAs is greater than three times more concentrated with Pb relative to MPb-LAs; therefore, we expect the substantial difference in soil Pb to necessitate more intensive reaction conditions and may be a product of the mass ratio of Pb to K-jarosite. Speciation for both untreated soils consists of different sorbed phases (*SI Appendix*, Table S3), but we do not expect sorbent

to be driving differences in reaction requirements given the weakness of Pb-surface sorption complexes at acidic pH. Other soil characteristics may also be driving difference in PLJ conversion (e.g., cation exchange capacity, clay mineralogy, etc.); however, Pb concentration remains the most likely dictator of increased reagent and/or severity of reaction conditions required for effective Pb remediation. We evaluated four additional soils of similar concentration to MPb-LAs, ranging from approximately 200 to 500 mg Pb kg⁻¹, and found PLJ conversion to meet or exceed 85% at room temperature which is closely aligned with results observed for MPb-LAs (*SI Appendix*, Fig. S3). Importantly, Pb concentrations of MPb-LAs are expected to be more commonplace for residential in situ remediation compared to the higher concentrations of HPb-HAs; therefore, high PLJ conversion efficacy at room temperature for MPb-LAs, along with the four additional soils of similar Pb concentration, is exceptionally promising for future residential remediation efforts.

Addition of K-jarosite was found to be critical to soil treatment methods maximizing conversion to low bioavailability PLJ phases. Treating soils with ferric sulfate in the absence of K-jarosite seed either did not induce PLJ formation or was considerably less effective than treatments where seed was present (Fig. 2 and *SI Appendix*, Table S3). HPb-HAs treated at 60 °C with no K-jarosite resulted in anglesite (PbSO₄) as the predominant Pb phase (53 ± 2.4%), a Pb species not expected to meaningfully contribute to decreased Pb bioavailability. PLJ conversion still occurred without K-jarosite seeding but to a substantially lesser extent compared (92% PLJ with seed compared to 24% PLJ without). MPb-LAs was similarly impacted by the absence of K-jarosite seed. More conversion to PLJ was observed when treated without seed (41 ± 1.6%) compared to HPb-HAs; however, a considerable increase in PLJ conversion resulted when utilizing K-jarosite seeding (85 ± 1.2%). We expect K-jarosite seeding to be critical as this may promote formation of additional jarosite-group minerals (i.e., PLJ) by acting as a nucleation site for similar minerals, facilitating the development of PLJ in the presence of Pb (17, 19, 27, 28). Additionally, Pb may be

substituting for K when K-jarosite is introduced at the treatment conditions presented. Jarosite-group minerals can undergo substitution reactions with other cations and oxyanions in model systems and partially substituted Pb has been found in jarosite-group minerals in natural environments (22–24, 28).

We observed K-jarosite seeding, at any application rate, to be critical to PLJ formation in soil. The influence of K-jarosite application rate on PLJ formation was assessed using HPb-HAs at two different reaction temperatures (40 and 60 °C) (SI Appendix, Tables S3 and S4). PLJ formation efficiency was enhanced at every rate of K-jarosite seed addition. Application of K-jarosite above 1.7 wt% had a diminishing effect and 1.7 and 3.3 wt% rates yielded similar results for both 40 and 60 °C treatments evaluated (~70% and ~95% PLJ, respectively) (see Fig. 3). For MPb-LAs, decreasing K-jarosite application to 0.8% wt for MPb-LAs did not have a significant impact on PLJ formation (SI Appendix). However, the absence of K-jarosite seed resulted in less than half of the PLJ to form compared to the seeded treatment (SI Appendix, Table S3), exemplifying the necessity of K-jarosite seed to facilitate effective Pb remediation.

Evaluating Influence of Jarosite Treatments on As Speciation. While efficacy of Pb treatment may be measured in PLJ conversion extent, As speciation is more varied (Table 1 and SI Appendix, Fig. S4). Post-treatment, all HPb-HAs samples possessed kankite ($\text{FeAsO}_4 \cdot 3.5\text{H}_2\text{O}$), an Fe(III) arsenate mineral similar to a more hydrated scorodite. Fe(III) arsenate minerals have historically been found to possess low bioaccessibility/bioavailability. Interestingly, all samples receiving K-jarosite were found to promote formation of beudantite ($\text{PbFe}_3(\text{OH})_6\text{SO}_4\text{AsO}_4$), a jarosite group mineral containing both Pb and As that, similar to PLJ, is highly resistant to destabilization at gastric pH conditions (42, 43). Formation of Fe arsenate minerals is unsurprising given the concentration of Fe(III) from added ferric sulfate and arsenate originating from the soil, especially while heated (44, 45); however, the presence of K-jarosite seeding appears to be critical to the formation of beudantite. K-jarosite may act as a nucleation site for further jarosite group mineral formation, explaining the observed formation of beudantite in the presence of K-jarosite and absence without (25, 26). Sorbed As species were present for all K-jarosite treated samples (39 to 54%) but decreased significantly relative to unamended HPb-HAs ($76 \pm 9.5\%$). Beyond speciation data, paired bioaccessibility results provide critical insight into the impact of the treatment.

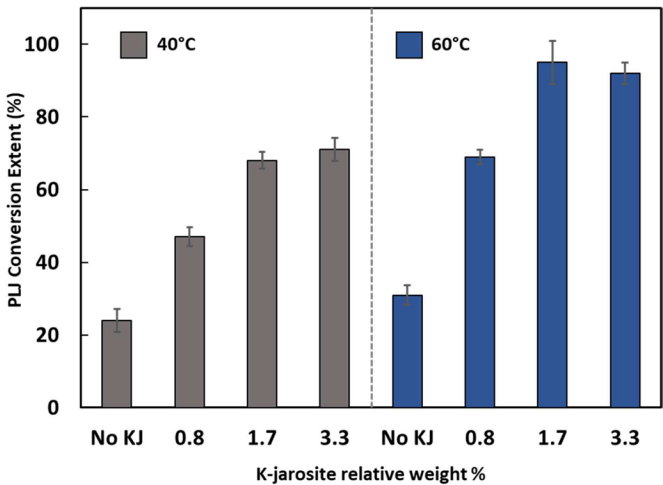


Fig. 3. Bioaccessibility results when performing K-jarosite treatment at increasing temperature or in the absence of K-jarosite (KJ) seed. Both soils were evaluated for Pb bioaccessibility percentage (A), whereas HPb-HAs was concurrently evaluated for both Pb and As bioaccessibility % (B). MPb-LAs contains low [As] (6 mg As kg⁻¹).

Dual Bioaccessibility Reduction of Pb and As Following K-jarosite Treatment. Jarosite-based treatments were highly successful at decreasing Pb and As bioaccessibility (Fig. 4 and SI Appendix, Table S3), signifying the only known in situ soil treatment to promote considerable bioaccessibility decreases of Pb and As through concomitant sequestration. Pb remediation efficacy of MPb-LAs was considerable even after a room temperature K-jarosite treatment (17.7%) (Fig. 4A). This result is in stark contrast to the high bioaccessibility of unamended MPb-LAs (79.4%), signifying an approximate 80% decrease in bioaccessible Pb. The new bioaccessible Pb concentration following treatment is 132 mg Pb kg soil⁻¹, making the soil suitable for residential areas as the EPA standard for Pb in bare soil play-areas is 400 mg Pb kg soil⁻¹. Additionally, K-jarosite treatment is exceptionally more effective than phosphate-based treatments which typically reduce Pb bioaccessibility by no more than 30 to 50% for soils of this concentration (13). Pb bioaccessibility for HPb-HAs also closely followed PLJ conversion extent but required soil heating to achieve similar results compared to MPb-LAs (Fig. 4A). Treatment

Table 1. Arsenic (As) speciation of HPb-HAs following K-jarosite treatment at different temperatures and K-jarosite seeding conditions

Soil	Arsenic EXAFS LCF				%IVBA	
	Treatment	Arsenic standard	Contribution (%)	R-factor	Pb	As
HPb-HAs: Pb arsenate pesticide source	40 °C	As(V) sorbed to Fe	39 ± 7.8	0.064	29.38	10.32
		Beudantite	31 ± 5.0			
		Kankite	30 ± 5.9			
	50 °C	As(V) sorbed to Fe	54 ± 11	0.081	10.85	10.64
		Beudantite	25 ± 5.5			
		Kankite	21 ± 10			
	60 °C	As(V) sorbed to Fe	52 ± 7.8	0.060	7.62	10.67
		Beudantite	35 ± 5.0			
		Kankite	13 ± 5.9			
	60 °C, no KJ seed	As(V) sorbed to Fe	70 ± 6.0	0.061	69.93	23.81
		Kankite	30 ± 6.0			
	Unamended	As(V) sorbed to Fe	76 ± 9.5	0.028	72.7	59.87
		Arseniosiderite	24 ± 6.6			

Speciation was determined using linear combination fitting of As EXAFS in k-space. R-factor is representative of the fraction of the sample spectra that was resolved by the reported fit. Pb and As in vitro bioaccessibility (IVBA) percentage, determined using EPA Method 1340, is also reported.

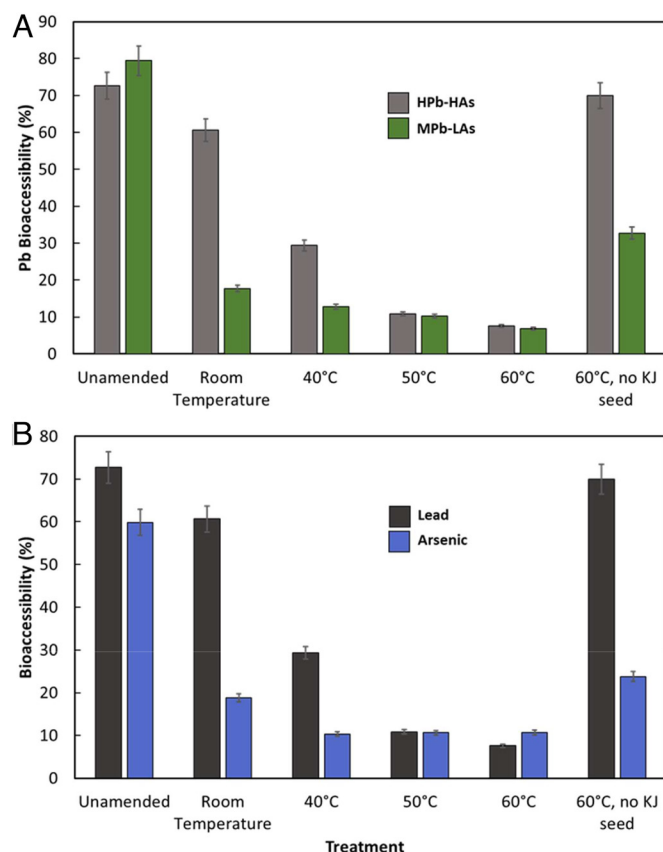


Fig. 4. Influence of KJ seeding rate on PLJ conversion for HPb-HAs. Relative weight % was calculated by dividing K-jarosite weight applied by the weight of the soil to be treated. Two soil treatment temperatures, 40 and 60 °C, were evaluated.

of HPb-HAs at room temperature saw slight reduction in Pb %IVBA (60.7% compared to 72.7% for unamended HPb-HAs) corresponding to minor conversion to PLJ ($16 \pm 1.7\%$); however, increasing reaction temperature to 40 °C and 50 °C resulted in successive, considerable decreases in Pb bioaccessibility (29.4% & 10.9%, respectively). Although HPb-HAs required soil heating for effective treatment, 40 °C still resulted in a 60% decrease in Pb bioaccessibility pre- vs post-treatment. This decrease is representative of an additional $1,036 \text{ mg Pb kg}^{-1}$ soil that is no longer available for solubilization at gastric conditions following treatment at 40 °C, significantly lowering exposure to soluble Pb and being well within the EPA's standard for non-play areas ($1,200 \text{ mg Pb kg}^{-1}$ soil). Soil heating to 50 °C may be achievable with the use of soil heating devices (e.g., heating probes, soil steaming, etc.) if desired to meet site-specific remediation goals. Additionally, MPb-LAs and four additional soils were found to convert significantly to PLJ at room temperature (*SI Appendix, Fig. S3*); therefore, HPb-HAs may represent a more extreme

treatment scenario; however, field testing methods and influences of heterogeneous soils will be explored in the future.

Bioaccessibility of As was only evaluated for HPb-HAs ($369 \text{ mg As kg}^{-1}$) given the low soil As concentration (7 mg As kg^{-1}) of MPb-LAs (Fig. 4B and Table 1). Unlike Pb, As bioaccessibility decreased significantly after treatment at room temperature (18.8%) compared to 59.9% for unamended HPb-HAs. Increasing heat treatment to 40 °C resulted in lower As bioaccessibility (10.3%), but no change in As bioaccessibility was observed at temperatures greater than 40 °C. Therefore, temperature influences on treatment efficacy for As bioaccessibility were observed as less critical compared to Pb bioaccessibility. This is predominantly due to the formation of Fe arsenate, as identified via As EXAFS, which is also sparingly soluble in acidic gastric conditions but is less dependent on high temperatures to form than jarosite-group minerals (15, 45). Beudantite formation, likely promoted by the presence of K-jarosite seeding, is also influencing As bioaccessibility lower due to low solubility at acidic environments similar to PLJ (43); however, Fe arsenate formation is expected to be most critical as treatment was still effective without K-jarosite seed (24% As bioaccessibility). This is supported by Fe^{57} Mossbauer analysis (*SI Appendix, Fig. S5*) as post-treatment jarosite phases were confirmed to be present but were joined by other Fe phases.

Jarosite treatment of soil Pb and As was found to remain stable for at least 9 mo at water-saturated conditions (Table 2). Using HPb-HAs treated with K-jarosite at 60 °C, water-saturated soil adjusted to pH 4 and 7 for 9 mo were found to have Pb bioaccessibility of 2.0 and 9.8%, respectively, with both having As bioaccessibility of $\leq 1\%$. These results are supported by continued stability of PLJ at both pH conditions. Interestingly, the soil kept at pH 4 and room temperature fostered continued development of jarosite phases ($100 \pm 10\%$), potentially as initially formed jarosite group minerals age through Ostwald ripening processes (15). Continued formation of PLJ after the initial 16 h treatment is highly promising, as this provides evidence that the initial treatment may promote continued PLJ conversion over time. Therefore, future investigations evaluating longer reaction periods at nominal soil temperatures may increase flexibility of future field applications. At pH 7, the fraction of PLJ decreased by approximately 15%; however, only a 2.2% change in Pb bioaccessibility was observed. Combined with these conditions being non-ideal for jarosite-group minerals ($\text{pH} > 4$) and at saturation for the total 9-mo reaction period, these results are a promising showcase of the long-term utility of the proposed K-jarosite remediation. This is especially the case for As, where As bioaccessibility continued to decrease to less than 1%, suggesting continued development of poorly soluble Fe arsenate and/or beudantite phases (42–45). PLJ has been found in soils at basic conditions and combined with initial stability results following lime application, there is great potential for jarosite-phases to remain stable in soils at nominal pH conditions, potentially increasing in stability over time. However, jarosite-group minerals have complex weathering dynamics and require further stability testing for a decisive answer to its long-term stability in natural environments.

Table 2. Stability of plumbojarosite (PLJ) for a HPb-HAs that was initially treated using K-jarosite seeding at 60 °C

Soil	1 st derivative Pb XANES spectra linear combination fits				%IVBA	
	Stability conditions	Pb standard	Contribution (%)	R-factor	Pb	As
HPb-HAs	pH 4, 9 mo	Plumbojarosite	100 ± 10	0.003	2.0%	0.1%
	pH 7, 9 mo	Plumbojarosite	77 ± 0.8	0.002	9.8%	0.1%
		Pb adsorbed to Fe	23 ± 1.4			

Soil was potted and maintained at saturation for the length of the experiment.

Impact of K-jarosite Seeding Rate on Pb and As Bioaccessibility.

Dry-mixing K-jarosite was a critical component to effectively reduce Pb bioaccessibility for both soils, but its influence varied (Fig. 4A). Presence of K-jarosite was more critical to Pb bioaccessibility reduction for HPb-HAs (Table 2). For MPb-LAs, bioaccessibility decreased to 32.7% following treatment at 40 °C compared to 12.8% with K-jarosite seeding (3.3 wt%). While bioaccessibility reduction was less without K-jarosite, the resulting decrease is still considerable relative to unamended MPb-LAs (79.4%). This efficacy with and without K-jarosite seeding may provide future remediation options to other Pb-contaminated systems, as different Pb-contaminated areas may not require the maximum decrease in Pb bioaccessibility to reach bioaccessible Pb concentration goals for protection of human health. The impact of variable K-jarosite seeding on HPb-HAs was tested at two reaction temperatures, 40 and 60 °C (Fig. 3). The lower heat treatment, 40 °C, in the absence of seeding K-jarosite had a paltry response in which Pb bioaccessibility only decreased by approximately 3% from untreated control. However, treatment at 60 °C without K-jarosite seed, resulted in an additional 22% reduction in Pb bioaccessibility. Increased heat in the presence of the Fe(III) applied to the system likely promoted increased development of Fe(III) (oxyhydr)oxides that may have facilitated increased chemical and/or physical protection from Pb dissolution at gastric conditions. Increasing K-jarosite to at least 0.8 wt% K-jarosite provided increased PLJ formation, in-turn decreasing Pb bioaccessibility considerably. As discussed previously, HPb-HAs required increased temperature compared to MPb-LAs, potentially due to Pb concentration, resulting in K-jarosite having greater influence on PLJ formation and subsequent bioaccessibility decrease at 60 °C compared to 40 °C. No lower limit of K-jarosite seeding rate, other than absence, for MPb-LAs was determined (i.e., >0.8 wt%), as critical for jarosite mineral formation and will continue to be probed in preparation for field trials. Bioaccessibility of soil As was less influenced by the presence of K-jarosite, ranging from approximately 10 to 25% across all samples evaluated (Table 2). At the highest seeding rate, we observed As bioaccessibility was further decreased and, perhaps, can be explained by increased jarosite-group mineral formation that may partially sequester As as beudantite. Importantly, increased jarosite-group mineral formation, as PLJ or beudantite, in the presence of K-jarosite is reducing available sulfate added during the treatment process, potentially facilitating the reduction of As bioaccessibility via Fe arsenate mineral (e.g., kankite) formation due to decreased competition with sulfate (44).

Conclusions and Implications

Remediation of Pb and As using jarosite-based remediation methods provides rare examples of effective concurrent remediation of cationic and oxyanion contaminants, making the new treatment methods exceptionally promising. K-jarosite seeding paired with ferric sulfate at either room temperature or 40 °C resulted in highly successful Pb and As remediation through the formation of low gastric solubility jarosite phases (i.e., PLJ and beudantite) or Fe arsenate (i.e., kankite) phases. Pb bioaccessibility decreases resulting from K-jarosite treatments are substantially more than other common alternatives (e.g., phosphate-based treatments) (13, 20). Both Pb and As bioaccessibility remained stable for at least 9 mo at pH 4 and 9 following K-jarosite treatment, suggesting that long-term stability after pH adjustment is achievable to return soils to agronomic conditions for turf growth. The reduction of As bioaccessibility is especially important because in situ soil remediation treatments that treat Pb, such as phosphate treatments, typically facilitate increased mobility of As via competitive sorption

effects (13). Addition of Fe is likely most critical to As bioaccessibility decreases via Fe arsenate formation, whereas jarosite-group mineral formation is essential for Pb treatment. Ultimately, the requirements of soil treatment are likely dependent on Pb and/or As concentration. While reactions at higher Pb concentrations (>2,000 mg Pb kg⁻¹) may require heating to 40 °C, relatively lower concentrations more typical of contaminated residential areas (<1,000 mg Pb kg⁻¹) are expected to require less stringent reaction conditions. This is supported by four additional soils (<500 mg Pb kg⁻¹) that were found to convert to PLJ at room temperature to a similar extent as MPb-LAs (*SI Appendix*, Fig. S3). For soils >1,000 mg Pb kg⁻¹, usage of affordable options for increasing soil temperature during treatment, such as using plastic soil covers during summer months, may expand availability of this technique to areas with limited economical resources. Continued evaluation of reaction parameters in field conditions is needed to build upon this work to account for climate-driven wetting and drying cycles and soils of diverse mineralogy and chemistry.

Research presented here paves the way for future field experiments that are currently being developed at the U.S. EPA. Particularly motivating is the potential opportunity to simultaneously treat Pb and As, and perhaps other cationic and anionic contaminant elements. This not only allows for areas that are dually contaminated to be treated via one methodology, but also protects against potential mobilization of oxyanion contaminants (e.g., arsenate) when applying methods that sequester Pb. Contaminant immobilization post-treatment likely extends to reductions in contaminant leaching from soils and into groundwater but will require further analyses to confirm. Potted soil experiments presented here are the precursor to field experiments which may enable cost-effective, in situ treatment of contaminated soils. Currently, excavation is the most common method for remedying soil contamination which costs millions of dollars per acre (46) and may have permanent ramifications on soil health. Performing in situ jarosite-based treatments may be performed at a fraction of the costs while removing the need for environmentally damaging excavation. While moderate soil heating may be needed for highly contaminated soils, future field treatments will remain in situ via either the use of soil heating implements (e.g., heating probes, soil wrapping, etc.) and/or utilizing a longer reaction time, as additional jarosite phases will likely continue to nucleate over time. Roto-tillage of K-jarosite to at least 7.5 cm soil depth followed by dissolved ferric sulfate application is a potential pathway for field application; however, specific field methods will be identified in the future with further experimentation. The proposed treatments may also benefit from surface barrier additives, such as compost or addition of clean topsoil used as a cap, further decreasing potential hand-to-mouth contact with soil. Most importantly, results presented here will serve as a foundation for future jarosite-based remediation of contaminated soils, substantially reducing exposure to Pb and As.

Data, Materials, and Software Availability. Research data have been deposited in data.gov (47). Additionally, all study data are included in the article and/or *SI Appendix*.

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