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Bioaccessibility, release kinetics, and molecular speciation of arsenic and lead in geo-dusts from the Iron King Mine Federal Superfund site in Humboldt, Arizona

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Abstract

Mine tailings contain multiple toxic metal(loid)s that pose a threat to human health via inhalation and ingestion. The goals of this research include understanding the speciation and molecular environment of these toxic metal(loid)s (arsenic and lead) as well as the impacts particle size and residence time have on their bioaccessibilty in simulated gastric and lung fluid. Additionally, future work will include smaller size fractions (PM_{10} and $PM_{2.5}$) of surface mine tailings, with the goal of increasing our understanding of multi-metal release from contaminated geo-dusts in simulated bio-fluids. This research is important to environmental human health risk assessment as it increases the accuracy of exposure estimations to toxic metal(loid)s.

Keywords

arsenic; geo-dust; human health; lead; mine tailings; simulated gastric fluid (SGF); simulated lung fluid (SLF)

Introduction

Arizona has approximately 60,000–100,000 abandoned or inactive mining sites. Mine tailing disposal sites in arid areas like Arizona are susceptible to wind erosion and become sources of airborne particulate matter or geo-dusts. These particles comprise contaminants like arsenic and lead, that are listed in the Agency for Toxic Substances and Disease Registry's Priority List of Hazardous Substances and are detrimental to human health (1–4). Additionally, climate models predict that Southwestern US will become increasingly warmer and drier, thus potentially increasing the harmful effects of these airborne metal(loid) contaminants (5, 6).

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In the current study, we employed an in vitro bioaccessibility method for the simulated gastric fluid (SGF) based on a standard operating procedure developed by Solubility/Bioavailability Research Consortium (SBRC) for arsenic and lead. The simulated lung fluid (SLF) method used a modified Gambles' solution developed by Takayka (7–13). Bioaccessibility is determined based on metal release normalized to total metals determined from Aqua Regia extraction. Bioaccessibility studies provide valuable information regarding chemical reactions that occur between particles and bioassay fluids and can measure the solubility of metal(loid)s in SGF and SLF (14).

X-ray absorption fine structure spectroscopy (XAFS) is one of few methods that can provide structural and compositional information on most types of cations and anions sorbed at solid-solution interfaces. XAFS can provide information on the speciation of selected cations and anions in complex mixtures of phases, including sorbed species like metal(loid)-contaminated soils (15). Sample solutions were isolated by allowing the suspensions to settle, and then filtering them at 0.45 μm. The residual solid was lyophilized and analyzed at the Stanford Synchrotron Radiation Light Source (SSRL) to determine changes in the oxidation states of As and Fe and determine their local bonding environment. Additionally, scanning electron microscopy (SEM) imaging was conducted to elucidate changes in particle size and shape in unreacted and post-extraction solid samples.

Materials and methods

This research utilized a homogenized surface mine tailings sample from Iron King Mine to achieve the following: i) identify the particle size impact on arsenic and lead bioaccessibility, ii) determine the relative bioaccessibility of arsenic in SLF and SGF, and iii) determine the molecular speciation via post-extraction analysis of the remaining sample solid using synchrotron-based XAFS and X-ray absorption near edge structure (XANES) as well as X-ray fluorescence (XRF). Bioaccessibility was determined based on the total metals determined from a lithium metaborate/tetraborate fusion with inductively coupled plasma mass spectrometry detection (ActLab, Ontario, Canada). Several NIST quality control samples were analyzed to confirm precision.

Mine tailing surface samples were collected and sieved to obtain size fractions relevant to ingestion (150 μm) and then eventually includes inhalation relevant mine tailing size fractions (≤10 μm, PM_{10} and $PM_{2.5}$). The 150 μm mine tailings were separated via metal sieving and then treated with SGF and SLF to determine the bioaccessibility of arsenic and lead. The bulk mine tailings surface sample (top 25 cm) were sieved to 150 μm and homogenized for the University of Arizona Superfund Research Program (SRP).

Samples were prepared in triplicate, covered to minimize light exposure, agitated at 60 rpm, and incubated at 37°C to simulate particle residence in the human gastric or lung system. Kinetic studies of the SRP group sample included ten resident times ranging from short (30 s time steps) to long (7 day) exposure time steps. These residence times were selected to a) develop the times relevant to particle resident times in the gastric (1 h) and lung (7 day) systems and b) gain an understanding of the release rates of metal(loid)s in these systems.

We hypothesized that (i) the smaller the particle size (i.e., the greater the surface area) the more accelerated the kinetics of arsenic and lead release would be, that (ii) bioaccessibility is a predictable function of the local contaminant-bonding environment as revealed from spectroscopy, and that (iii) an increase in pH and the composition of the SLF (i.e., the presence of phosphorus in SLF) can reduce the amount of arsenic present in the solution.

Results

Total bioaccessible metals are greater in the SGF than in SLF; moreover, release is maximized at 100 h in the SGF and at 15 min in the SLF (Figure 1). SEM images show an unreacted bulk mine tailing sample as well as a sample reacted in SGF at 1 h and in SLF at 48 h. The SGF reacted image illustrates aggressive dissolution of particles at 10 μm. The SLF image, also at 10 μm, illustrates small crystal particles that have likely reprecipitated from solution into the analyzed solid (Figure 2). The XRF microprobe analysis shows the physiochemical change from the unreacted tailings to the SGF reacted tailings, where As(V) is initially mostly associated with ferrihydrite, a hydrous ferric oxyhydroxide (as an adsorbed species determined by XAS, data not shown), and after reaction in SGF As(V) is associated with jarosite, a hydrous iron sulfate acting either as a surface complex or a stoichiometric component (Figure 3).

Discussion

The larger release of arsenic and lead ions into the SGF solution is consistent with the much more acidic pH (1.5) of the SGF, relative to SLF, condition. The SLF (pH 7.4) allows for a lower fraction of metal(loids) to be released. The release of metal(loid)s in the SGF peaks at 100 h, which is much later than the 1 h extraction time recommended in the EPA Standard Operation Procedure for an In Vitro Bioaccessibility Assay for Lead in Soil. The residence or extraction times for an SLF bioaccessibility assay have yet to be recommended by the EPA because particle sizes greatly influence residence time in the lung (16, 17). The current study found that the metal(loids) maximized well before a 1 h extraction time at 15 min (SLF) and well after at 100 h (SGF). Therefore, if a standard EPA bioaccessibility methodology is utilized for either an SGF or SLF bioassay, a 1-h residence time would grossly underestimate the amount of bioaccessible arsenic or lead one would be exposed to (16).

Conclusions

ICP-MS data indicate that resident extraction times, pH, and bioassay mineral composition are all important indicators of bioaccessibility. In addition, iron, arsenic, and lead concentrations in the SGF bioassay display greater concentrations than those in the SLF bioassay, which is likely due to the decreased pH (3, 5, 18). It is generally agreed that iron oxides are the dominant soil constituents responsible for arsenic sorption (31). However, arsenic sorption has also been shown to be correlated to aluminum oxides and soil or clay content. In this regard, further study is needed to understand the lack of As-Fe correlation in the kinetic release data (3, 19, 20). The SLF bioassay that contains salts and phosphates illustrates an interesting kinetic release curve with an initial metal(loid) release (15 min), a re-precipitation or sorption phase, and another smaller release (post 48 h) (Figure 1). This may be due to the formation of new phases that precipitate iron or aluminum hydroxyl sulfates, or the arsenic desorption that may have been driven by phosphates present in the solution (3, 21). XAFS data indicated that no change in oxidation state of As(V), the predominant form in soil, occurred. This is important because As(V) is the less toxic form of environment from soil to human health.. arsenic, given that As(III) is more soluble and, therefore, bioavailable (3, 18–20, 22–26, 30). The XRF data also indicated that iron is undergoing a change from ferrihydrite to jarosite in the gastric bioassay. Additionally, arsenate has been known to substitute for sulfate in jarosite and could be the reason there is a similar loss of arsenic and iron in the SGF after 100 h (29).

Tailings in arid and semi-arid climates may present a greater human health risk associated with direct particulate exposure from fugitive dusts. It has been observed that the bioavailability of metals in tailings is controlled by metal speciation, not total mass concentration. The bioaccessibility of these dusts varies with temporary and simulated target organ exposure. Finally, secondary mineral precipitation, observed with SEM (and XRD, not shown), may play an important role in the availability of surface sites for re-adsorption of released contaminants. Additionally, given that particle size is a driving factor in bioaccessibility inhalation, relevant mine tailing particulate matter (PM_{10} and $PM_{2.5}$) are currently being conducted and will be published at a later date (17, 27, 28).

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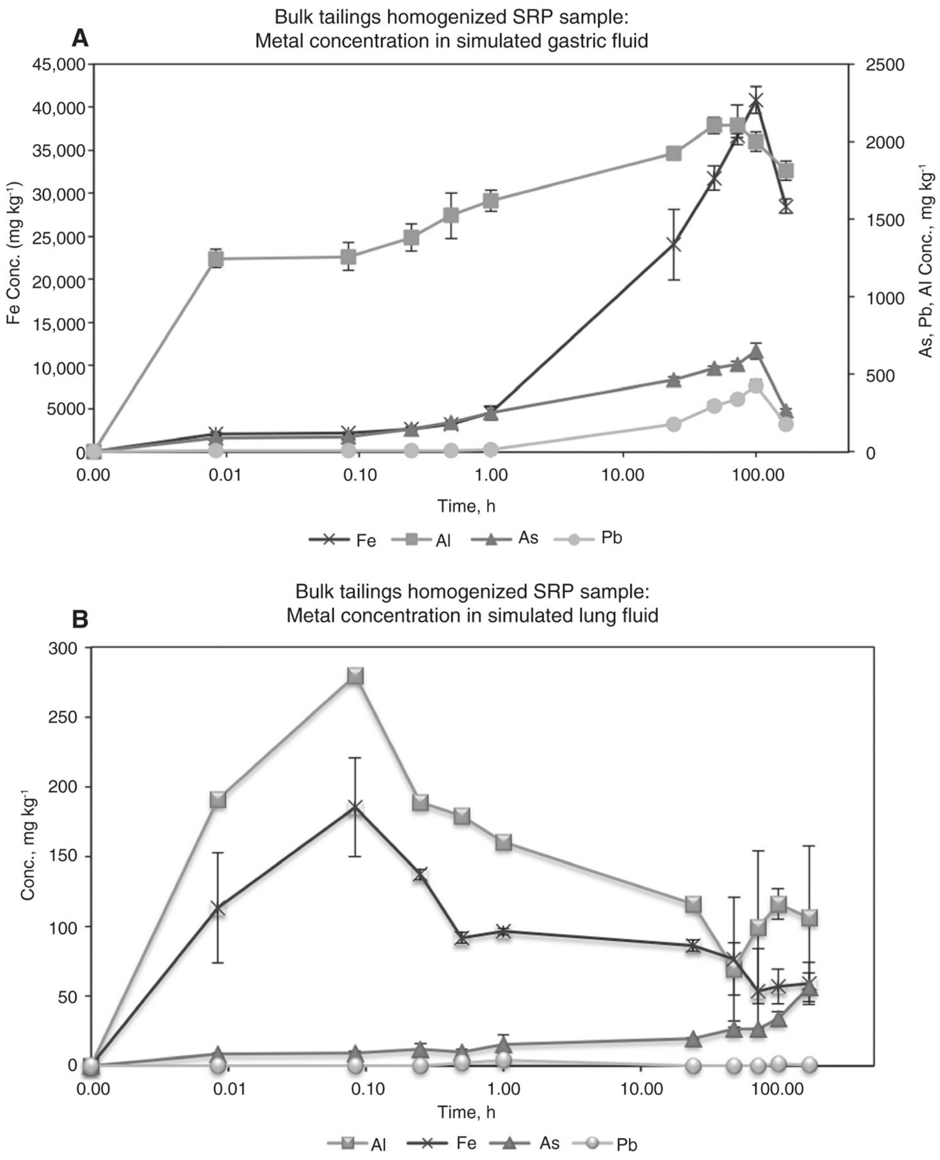

Figure 1.

Bulk tailings homogenized SRP sample: metal concentration in SGF.Bulk tailings homogenized SRP sample: metal concentration in SLF.

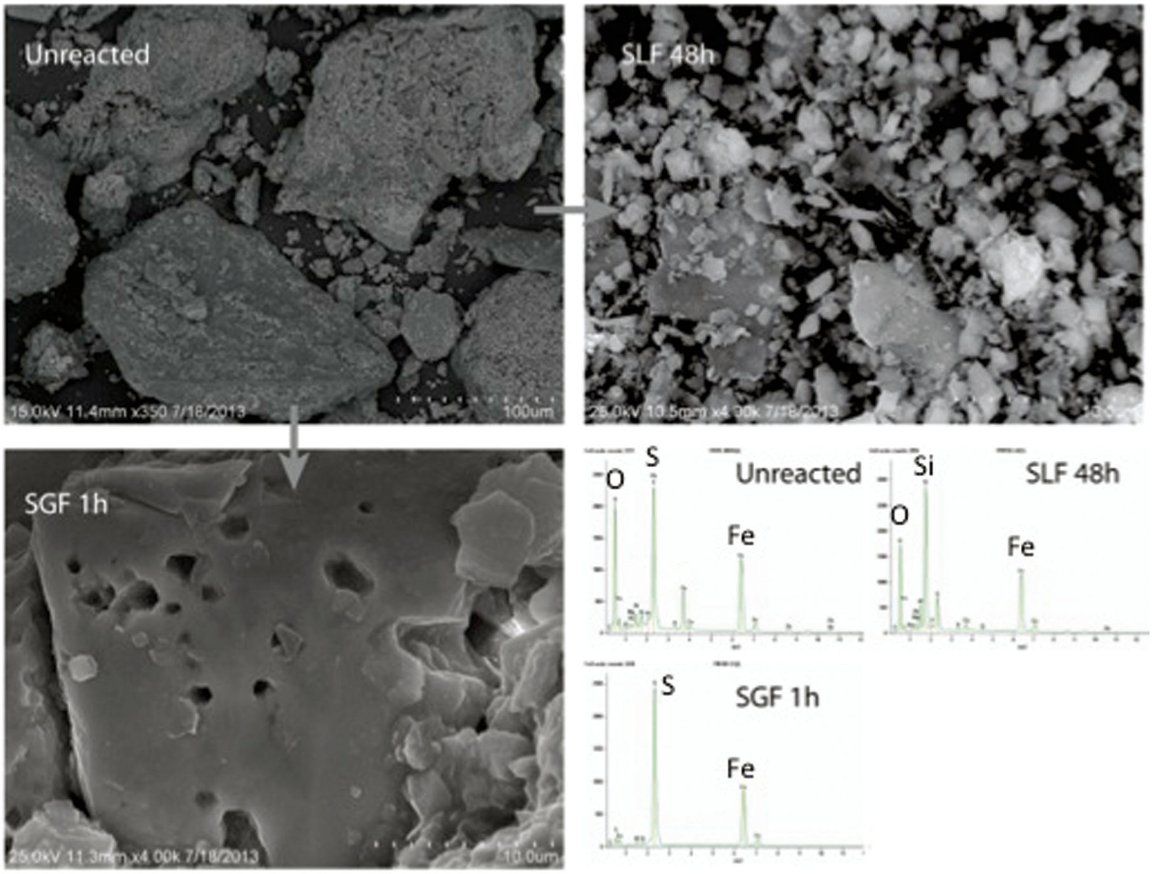

Figure 2.
SEM imaging of unreacted mine tailings sample, SLF for 48 h (top right), SGF for 1 h (bottom left), and corresponding EDS data.

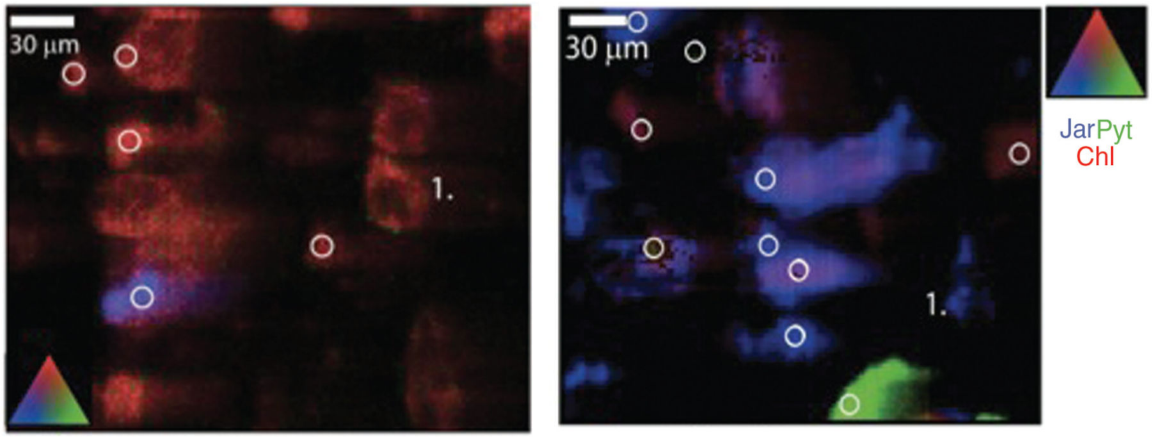

Figure 3.

Fe XRF images of unreacted mine tailings (left), SGF 24-h extracted samples (a phase shift from from ferrihydrite to jarosite occurred after 24 h).