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Assessment of arsenic speciation and bioaccessibility in mine-impacted materials

Cameron J. Ollson[a,*], Euan Smith[a], Kirk G. Scheckel[b], Aaron R. Betts[b], Albert L. Juhasz[a]

[a] Future Industries Institute, University of South Australia, Mawson Lakes, SA 5095, Australia
[b] United States Environmental Protection Agency, National Risk Management Research Laboratory, Land Remediation and Pollution Control Division, Cincinnati, OH 45224-1701 USA

HIGHLIGHTS

- Different mine materials have statistically dissimilar As bioaccessibility values.
- As bioaccessibility is dependent on As and Fe speciation and particle size.
- As: amorphous Fe molar ratio describes As bioaccessibility in calcinated materials.
- Default RBA values may not be appropriate for different mine-impacted materials.

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ABSTRACT

Mine-impacted materials were collected from Victoria, Australia and categorized into three source materials; tailings (n = 35), calcinated (n = 10) and grey slimes (n = 5). Arsenic (As) concentrations in these materials varied over several orders of magnitude (30–47,000 mg kg^{-1}), with median concentrations of 500, 10,800 and 1500 mg kg^{-1}, respectively. When As bioaccessibility was assessed using the Solubility Bioaccessibility Research Consortium (SBRC) assay, As bioaccessibility ranged between 4 and 90%, with mean gastric phase values of 30%, 49% and 82% for tailings, calcinated and grey slimes, respectively. An analysis of variance (ANOVA) determined that As bioaccessibility was significantly different ($P < 0.05$) between source materials. This was due to differences in As mineralogy, soil particle size as well as the concentration and nature of Fe present. X-ray Absorption Near Edge Structure (XANES) analysis identified arseniosiderite, yukonite, realgar, loellingite and mineral sorbed arsenate species in mine-impacted materials. Despite differences in physicochemical properties, 'mine wastes' are often reported under a generic descriptor. Outcomes from this research highlight that variability in As bioaccessibility can be prescribed to As mineralogy and matrix physicochemical properties, while categorizing samples into sub-groups can provide some notional indication of potential exposure.

1. Introduction

Historic gold (Au) mine sites exist throughout the world as a result of legacy activities. These sites are numerous and are typically associated with elevated concentrations of arsenic (As) due to the association of both As and Au with sulphidic phases in primary ores. Arsenic contamination at former mine sites is a consequence of Au extraction processes which result in three predominant matrices; tailings, calcinated and grey slime materials. Tailings are typically associated with the refuse material from crushing processes that separate valued minerals from ore. Calcinated materials are waste products resulting from high temperature treatment applied to Au-bearing ores that facilitates thermal decomposition, phase transition, removal of volatile fractions and Au recovery. In contrast, grey slimes are silty material that result from the beneficiation process of separating minerals from ore. Slimes are fine material predominantly collected from the bottom of settling tanks that are used to separate minerals from ore after the crushing process.

As a consequence of physical and thermal processes for the extraction of Au, As mineralogy, concentration and other physicochemical properties of the contaminated matrix may vary which may impact on human health exposure assessment. Previous research has evaluated As bioaccessibility from these three mine-impacted materials; however, despite their different properties, it

* Corresponding author.
E-mail address: cameron.ollson@mymail.unisa.edu.au (C.J. Ollson).

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is often reported under a generic descriptor, i.e. mine waste [1–7]. Utilisation of a generic descriptor may lead to the misrepresentation of As bioaccessibility in individual mine-impacted materials, and therefore impact on human health exposure assessment. This generic descriptor has also lead to the adoption of single default relative bioavailability (RBA) values for As by regulators which may not be sufficiently protective of communities within As contaminated areas. For example, a region-specific As RBA value of 33% has been adopted for historic tailings in the gold mining region of Victoria, Australia (Meaklim personal communications). Other jurisdictions worldwide have adopted default As RBA values, such as the United States Environmental Protection Agency (US EPA; 60% for As contaminated soils) [8], although site-specific evaluation is recommended. The default value was generated based on As bioaccessibility data from a limited number of samples, despite the fact that other mining waste materials are present at sites that have different physiochemical properties compared to tailings materials, e.g. calcinated materials and grey slimes.

The purpose of this research was to (1) evaluate the bioaccessibility of As from multiple mine waste sources (tailing, calcinated and slime materials) using the Solubility/Bioaccessibility Research Consortium (SBRC) assay, (2) use X-ray Absorption Near Edge Structure (XANES) analysis to evaluate if mineralogy is responsible for differences in As bioaccessibility, (3) evaluate the differences in As bioaccessibility between the three materials by assessing the relationship between As bioaccessibility and both total and reactive iron (citrate dithionite extractable Fe), (4) determine if particle size can account for differences in As bioaccessibility, (5) assess the appropriateness of default values for As RBA by evaluating exposure for all mine-impacted materials.

2. Materials and methods

2.1. Mine impacted materials

Materials used in this study were collected from areas contaminated with As through activities associated with Au extraction and recovery. Surface materials (0–20 cm) were collected from locations impacted by tailings (n = 35), calcinated materials (n = 10) and grey slimes (n = 5) (Table 1). Following collection, materials were air dried then sieved to recover the <2 mm and <250 μm particle size fractions. The <250 μm particle size fraction was utilised for As bioaccessibility assessment as it is the upper sized particle fraction that is believed to adhere to the hands of children and is available for hand-to-mouth transfer [9]. Total metal/metalloid concentrations in the <2 mm and <250 μm particle size fraction was determined using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) following acid digestion using USEPA method 3051[10] in a Mars6 microwave (CEM).

In order to determine the concentration of reactive Fe (amorphous Fe and finely divided hematite and goethite) in the materials, citrate dithionite extractable Fe was undertaken using the method of Holmgren [11] with analysis by ICP-OES. Particle size analysis was performed on representative tailings, calcinated and slime materials using an Accusizer 780 Optical Particle Sizer. Particle size distribution was determined using Single Particle Optical Sensing (SPOS) or light obscuration to size particles. A 1 ml aliquot of sample material (0.1% w/v in Milli-Q water) was injected into the particle size chamber (containing 50 ml Milli-Q water) at a flow rate of 50 ml min^{-1}. Samples were analysed for 60 s with the results expressed as percentage contribution for four particle size ranges; 1 μm–25 μm, >25 μm–<50 μm, >50 μm–<200 μm, and >200 μm–<250 μm.

2.2. X-Ray absorption near edge structure (XANES) spectroscopy analysis

To represent each matrix, two samples of each material were analysed. The samples that were selected were representative of the range in concentrations within the three materials. Samples were ground with a mortar and pestle, pressed into a pellet and mounted on Kapton tape prior to XANES analysis at Sector 10-BM, Advanced Photon Source, Argonne, USA [12]. The storage ring operated at 7 GeV in top-up mode. A liquid N_2 cooled double crystal Si(111) monochromator was used to select the incident photo energies and a platinum-coated mirror was used for harmonic rejection. Calibration was performed by assigning the first derivative inflection point of the K-edge of sodium arsenate (11874 eV) [13] with simultaneous collection of the reference for each scan for calibration of sample spectra. Arsenic X-ray absorption spectroscopy (XAS) spectra were collected in triplicate at the As K-edge (11867 eV) in transmission and fluorescence using a 4-element Vortex florescence detector. Aluminum foil was used to cover the fluorescence detector window to suppress florescence from other elements (e.g. Fe) in the samples. Data analysis was conducted using Athena software [14]. Triplicate scans for each sample were merged, then normalized, and converted into *k* space. Linear combination fitting (LCF) was used to identify As speciation in the samples [13,15]. Linear combination fits (−30 to +30 eV relative to the calibration energy) were performed using XAS normalized and derivative μ(E) spectra from reference standards to identify As phases in the soil samples. During the LCF, components were only allowed to contribute to the model if the sum-square error was reduced by 20% [16]. The R-factor is a measure of the mean square sum of misfit at each data point and describes the degree of uncertainty in the fitting process [17].

Reference materials for As LCF included dimethyl arsenate, monomethyl arsenate, beudantite ($PbFe_3(AsO_4)SO_4(OH)_6$), arseniosiderite ($Ca_2Fe^{3+}{}_3(AsO_4)_3O_2{\cdot}3(H_2O)$), scorodite ($FeAsO_4{\cdot}2(H_2O)$), orpiment ($As_2S_3$), realgar ($As_4S_4$), arsenate sorbed to gibbsite ($Al(OH)_3$), arsenate sorbed to hematite (Fe_2O_3), arsenate sorbed to goethite ($\alpha-FeOOH$), arsenate sorbed to ferrihydrite, arsenate sorbed to birnessite (MnO_2), arsenite adsorbed to ferrihydrite, arsenite adsorbed to pyrite (FeS_2), arsenite sorbed to fougerite ($Fe^{2+}{}_3Fe^{3+}[(OH)_8]^+[Cl,\ H_2O]^-$), arsenite sorbed to mackinawite ($(Fe,Ni)S_{0.9}$), arsenite sorbed to siderite ($FeCO_3$), lollingite ($FeAs_2$), arsenolite (As_4O_6), yukonite ($Ca_7Fe^{3+}{}_{11}(AsO_4)_9O_{10}{\cdot}24.3(H_2O)$), arsenopyrite (FeAsS), and schneiderhohnite ($Fe^{2+}Fe^{3+}{}_3As_5O_{13}$). Data for LCF fits reveal As speciation in each soil as ratios of these mineral forms.

2.3. Assessment of As bioaccessibility

Arsenic bioaccessibility in mine-impacted materials was determined using the <250 μm particle size fraction and the gastric phase of the SBRC assay. This method is recommended by the US EPA based on strong statistical comparison to As relative bioavailability (RBA) determined using in vivo models [18–20]. Mine-impacted materials (n = 50; 3 replicates of each sample) were combined with gastric phase solution (30.03 g l^{-1} glycine adjusted to pH 1.5 with concentrated HCl) to achieve a soil:solution ratio of 1:100. Samples were incubated at 37 °C, 40 rpm on a Ratek suspension mixer for 1 h ensuring that the pH was maintained at 1.5. After gastric phase extraction, samples (10 ml) were collected and filtered through 0.45 μm filters for analysis by ICP-MS or OES. Arsenic bioaccessibility was calculated by dividing the gastric phase extractable As by the total soil As concentration (Eq. 1).

$$\text{As bioaccessibility}\,(\%) = \left[\frac{\text{In vitro As}}{\text{Total As}}\right] \times 100 \quad (1)$$