

Identifying Predictors for Bioavailability of Arsenic in Soil at Mining Sites

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ABSTRACT

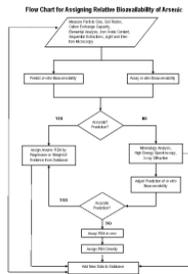
Assessing risks due to arsenic (As) in soil uses toxicity criteria based on exposures to As in drinking water, where bioavailability of soluble salts of arsenic is nearly 100%. Bioavailability of As in soil is usually much lower leading to an overestimation of risk. Site-specific relative bioavailability (RBA), the ratio of uptake of soil-bound As to As dissolved in water, can be determined with expensive *in vivo* feeding studies. Bioaccessibility is the *in vitro* counterpart of RBA, but it is not always predictive for the *in vivo* measurement. This research will identify geochemical and mineralogical parameters which control RBA of soil-bound As, and inexpensive bench procedures for estimation of RBA acceptable in a regulatory setting. Soils collected in Nevada County, CA, were analyzed for total metals and assayed for bioaccessibility of As using an *in vitro* gastrointestinal model. Bulk X-ray diffraction (XRD) and X-ray absorption fine structure spectroscopy (XAFS) were used to characterize mineralogical associations of As. As concentrations ranged from 9-9,700 mg/kg and bioaccessibility of As ranged from 1-44%. Plotting the log[As] vs. bioaccessibility suggested four populations. Arsenate (As⁵⁺) was the sole oxidation state detected, in all but one sample; As⁵⁺ is primarily associated with ferric (hydro)oxide (primarily rust suggests ferrihydrite). Preliminary estimates of amorphous content did not correlate with mineralogical association or bioaccessibility. The wide range of values for bioaccessibility and metal content are adequate to identify gradients and correlations. Further analysis of soil by differential XRD, μ -XRD, μ -X-ray fluorescence, and μ -X-ray absorption will provide chemical and spatial information about the minor mineralogical phases and bioaccessibility of As.

INTRODUCTION

Mine Scarred Lands (MSL) in California are a major threat to human health and the environment and a major challenge for Brownfields revitalization. The California Department of Conservation has identified 47,000 abandoned mines in California. These MSL present threats to human health and the environment from arsenic, mercury, other heavy metals, acid mine drainage, and physical hazards. DTSC has been involved with the cleanup of MSL for many years. At most of these sites, arsenic is the number one threat to human health. Due to the high cancer potency of arsenic, sites are often required to be cleaned up to background concentrations and thus MSL site cleanups are often unnecessarily conservative. Animal studies could be conducted at each site but the costs are prohibitive. This research is evaluating the relationship between the geochemistry of bioavailability of arsenic to develop cost-effective analyses that can result in more cost-effective MSL cleanups.

METHODS

Soil samples were collected at the Empire Mine State Historic Park in Nevada County, California. Sample locations were chosen in the field based on association with various mine features and As concentration as measured by field X-ray Fluorescence (XRF). Field activities were performed by DTSC in conjunction with USGS. Total metal analysis was later completed using US EPA Method 6010. Samples were sieved to <250 μ m in the laboratory of Dr. Kim at Chapman University and distributed to the various investigators for analysis. Dr. Basta at Ohio State University measured As bioaccessibility using an *in vitro* gastrointestinal model. Dr. Foster with USGS analyzed samples using X-ray absorption fine structure (XAFS) at the Stanford Synchrotron Radiation Lightsource (SSRL). XAFS is an element-specific probe of molecular-level atomic structure. Using this technique, allows the determination of oxidation state(s) and the semi-quantitative assignment of mineral species of As species. This is achieved using model-independent and model-dependent assessment techniques (principal component analysis and linear combination fits, respectively).



Arsenic *in vitro* Bioaccessibility

In vitro Gastrointestinal Method:

Gastric Phase

- 0.1M NaCl, 1% Pepsin
- 1:150 soil:solution ratio
- Manual adjustment with HCl to pH 1.8 with constant stirring for 1 hr.

Intestinal Phase

- 0.563 g Bile, Pancreatin added
- Manual adjustment with Na₂CO₃ to pH 1.1 with constant stirring for 2 hrs.

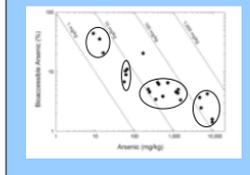


Figure 1: Bioaccessibility of Arsenic using an *in vitro* Gastrointestinal (IVG) Method: The IVG performed at Ohio State University method revealed that our samples had a range of As bioaccessibility from 1-44% of the total As. Plotting Log [Total As] vs. Log bioaccessible Arsenic suggests 4 populations of samples with a single outlier (From the Sand Dam Area).

Arsenic Fractionation by Sequential Extraction

Fraction	Extractant	Target Phase	Conditions	Sample E16 Results
1	0.05 M (NH ₄) ₂ SO ₄	Non specifically adsorbed As	4 hr shake @ 20°C	8 mg/kg 0.08%
2	0.05 M NH ₄ H ₂ PO ₄	Specifically sorbed As	16 hr	235 mg/kg 2.4%



Figure 2: Geographical distribution of As concentrations and bioaccessibility as measured in samples obtained from Empire Mine State Historic Park in Nevada County, California.



Diabase rock found along Powerline Trail showing iron oxide staining and weathering

High energy synchrotron-based X-ray Analysis

SSRL operates at a voltage of 3.0 GeV and 200-1000 mamp. In preparation for XAFS data collection, samples were air-dried and approximately 2 grams of each sample was added to a plastic microcentrifuge tube containing a polystyrene bead (approximately 2 mm diameter). A high-speed shaker was employed to pulverize the samples to a flour-like consistency. Natural and synthetic samples of iron oxides, iron oxyhydroxides, and arsenic-bearing phases (both X-ray amorphous and crystalline) were obtained from various sources and/or synthesized in Dr. Foster's laboratory. These samples were carried through the same preparation and analysis procedures as the soil samples. Approximately 0.5 g of each pulverized sample was front-loaded into a 3-millimeter thick Teflon holder enclosed on both sides with kapton tape. The energy range for As K-edge XAFS spectra was 11.630-12.630 KeV. The time required for collection of a single As scan is ~30 minutes; in practice, several successive scans are usually collected and averaged together to improve the signal-to-noise ratio. Typically 2-6 scans were averaged to obtain good-quality XAFS data from natural samples.



Arsenic X-ray Absorption Fine Structure (XAFS)

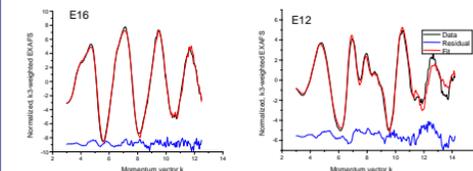


Figure 3: Representative As XAFS spectra. Samples were run in conjunction with model compounds. The black lines are the spectra of the sample and the red line the spectra of the best fit model compound. A) All but one sample had spectrum best fit with As⁵⁺ associated with ferrihydrite. B) The single outlier (E12) is composed of 60% arsenopyrite (FeAsS).

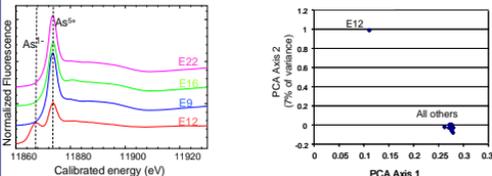


Figure 4: As X-ray Absorption Near Edge Structure (XANES) Spectra: Arsenate (As⁵⁺) was the sole oxidation state detected in all but one sample. The secondary peak depicted in the blue line is indicative of a reduced As species with a nominal valence of approximately -1

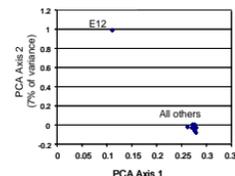


Figure 5: Plots of Principal Component Analysis Eigenvalues: The proximity of sample points is directly proportional to the similarity of their representative XAFS spectra

SUMMARY

Summary of Data for Sample E16

Mineralogical Feature	Waste Rock Pile
Total Iron (mg/kg)	75,800
Total Arsenic (mg/kg)	9,600
As Oxidative State	Arsenate (As 5+)
As Mineralogical Association	Ferrihydrite
IVG Bioaccessible As (% Total As)	1.62
F1+ F2 Bioaccessible As (% Total As)	2.5



CHALLENGES IN THIS PROJECT:

- Identifying bridges between mineralogy and wet chemistry
- Deciding which materials to test *in vivo*
- Dosing swine with very low RBA materials
- Reducing mineralogical, spectroscopic, and crystallographic data to continuous or categorical variables suitable for predictive models, e.g. regression

CHALLENGES FOR THE FUTURE:

- Mineralogical regimes with low Fe content
- Comparison of animal models: monkey, swine, mouse
- Inhalation RBA *in vivo* and *in vitro*

REFERENCES:

- Basta, N.T., J. N. Foster, E.A. Dayton, R. R. Rodriguez, and S.W. Casteel. 2007. The effect of dosing vehicle on arsenic bioaccessibility in smelter-contaminated soils. Invited manuscript for the special JEHSP publication "Bioaccessibility and human bioavailability of soil contaminants". J. Environ. Health Sol. Part A. 42:1275-1281.
- George, G.N., and Pickering, I. J. (1993). "EXAFSPAK: A suite of programs for the analysis of x-ray absorption spectra". Stanford Synchrotron Radiation Laboratory (freeware).
- <http://ssrl.slac.stanford.edu/exafspak.html>
- Kelly, S. D., Hesterberg, D., and Ravel B. (2009). "Chapter 14: Analysis of Soils and Minerals using X-ray Absorption Spectroscopy". In *Methods of Soil Analysis, Part 5. Mineralogical Methods*. SSSA Book Series, 78 p.
- Wenzel, W.W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., Adriano, D.C., 2001. Arsenic fractionation in soils using an improved sequential extraction procedure. *Analytica Chimica Acta* 436 (2001) 309-323.
- Whitacre, S. D. 2009. M.S. Thesis. Soil controls on arsenic bioaccessibility: Arsenic fractions and soil properties. The Ohio State University, Columbus, OH.

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