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Direct Arsenic Speciation in Soils using Macroscopic and Micro-focused Spectroscopic Techniques

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Beamline(s): X26A

Introduction: Soil contamination with arsenic (As) may have different origins: mining, agricultural and industrial pesticide application, smelting operations, and naturally occurring dissolution phenomena of As bearing minerals, to name a few. Concomitantly, other contaminants such as lead (Pb), copper (Cu), zinc (Zn), and chromium (Cr) may be largely abundant in soils where As contamination is prevalent and of concern. These co-contaminants may significantly influence the speciation of As in soil environments, because adsorption sites on iron, aluminum, and manganese oxides are preferable sites of adsorption for all of the aforementioned ions (Arai, Elzinga et al. 2001; O'Reilly, Strawn et al. 2001). In order to determine the effects of commonly occurring metal contaminants in contaminated soils on As speciation, the objectives of our experiments at X26A were to determine the redox species of As in soils of differing As contamination history and to determine the elemental distribution of As and other concomitant metals.

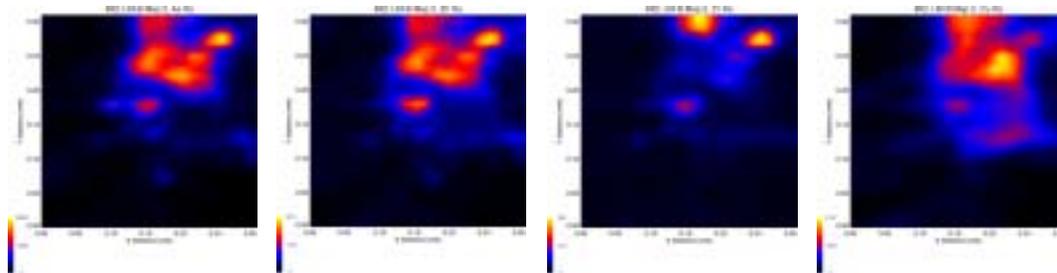
Methods and Materials: Two arsenic contaminated soils were obtained of varying geographic origin and differing arsenic application history: Soil 1 (LM) was heavily contaminated with copper chromated arsenate and Zn, Soil 2 (FP) received extensive applications of lead-arsenate. Whole soils and thin sections (30 μ m polish) of the soils were investigated at X26A using the beamline's μ -x-ray fluorescence (μ -XRF) elemental mapping and μ -x-ray absorption near edge structure (μ -XANES) spectroscopy capacities. A beam size of 15 μ m was chosen

Results: In LM soil, we determined that As occurs in discrete agglomerations, which strongly coincide with Zn. Other coincidences were noticed with Cu, Cr, and Fe, however, Zn and As hotspots were near mirror images of themselves. This occurred despite the fact that Cu concentrations were nearly twice as high as those of Zn. Micro-XANES spectroscopy established that As (V) is the dominant As redox species.

In FP soil, As occurred more sequestered than in LM soil over a mixed Fe-Mn matrix. Despite the high Pb concentrations, little or no association between Pb and As were established from μ -XRF elemental maps. Arsenic hotspots did coincide with hotspots of Fe and Mn in close spatial proximity. Arsenate was the dominant As redox-species in the FP soil.

The association of As with metal cations in soils such as Zn, Cu or lead appears to be closely related to soil pH and organic matter content. The LM soil has a pH of 7, while the FP soil's pH is 4.5 and appears to be largely buffered by a high organic matter content. Future μ -EXAFS spectroscopy will contribute additional information about the speciation of As in these contaminated soils.

References: Arai, Y., E. J. Elzinga, and D.L. Sparks (2001). *J. Colloid Interf. Sci.* **235**(1): 80-88. O'Reilly, S. E., D. G. Strawn, and D.L. Sparks (2001). *Soil Sci. Soc. Amer. J.* **65**(1): 67-77.



200 μ m x 200 μ m maps of LM subsurface soil. **From left to right:** As, Zn, Cr, and Cu. Yellow color indicates highest concentration. Intensities vary per map