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Arsenic Speciation in a Lead-Arsenate Contaminated Orchard Soil

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Beamline(s): X26A

Introduction: Recent investigations at beamline X26-A at the NSLS were centered on the identification and speciation of arsenic (As) phases in a lead-arsenate contaminated orchard soil (pH ~ 4.5) using μ-XRF and the newly improved μ-XANES features. The fate and mobility of both arsenate (AsO_4^{3-}) and lead (Pb^{2+}) are of great environmental and public concern, because of their toxicity and carcinogenic properties to mammals.

Methods and Materials: Micro-XRF maps were collected on whole soil samples from two different depths (FP 10-A = 0-20cm, FP 10-B = 20 – 40cm) to identify the major elemental associations in 2D space. The beamsize was 15x15μm with average ų-XRF maps of 0.4x0.4mm and a pixel size of 15x15μm with integration times per point of 5 to 8 sec. From previous work, we know that As and Pb tend to occur together in this soil. Spectroscopically, the As Kα-1 x-ray emissions signal is overlapped by the Lα-1 emissions signal of Pb and, hence, difference maps have to be made. Alternatively, only the Kβ-1 and Lβ-1 x-ray emissions signals of As and Pb, respectively, may be recorded for 2D imaging. In order to observe any Pb, however, the energy of the incident x-ray beam must be at or above the Pb L-III edge (13 035 eV). In this run, we carefully noted the boundaries of our maps and recorded the fluorescence signal for As only in order to collect subsequent As K-edge x-ray absorption near edge spectroscopic data on As hotspots.

Results: The ų-XRF mapping data shows that As appears mostly as a spread out, diffuse mass. In places where it does concentrate (e.g. FP 10-A fine map 1), the As hotspot is overlapped by iron and to some extent by zinc (Zn) (Figure 1). In the FP 10-B soil, As also appears as a diffuse mass, which co-occurs with iron as well, but is not as apparent as in the FP 10-A fine map 1. While in the surface soil (FP 10-A) the As hotspots appear as round discs, there is no distinct 2D shape to the As hotspots in the subsurface soil (FP 10-B).
The normalized XANES data (Figure 2) show that As in the hotspots of FP 10-A and 10-B occur as the pentavalent redox species (As +5). The features in the XANES region suggest that no precipitate like lead-arsenate phases exist, as the distinct features of schultenite and $PbHAsO_4$ salt are missing. The XANES data have some resemblance to the features of the scorodite XANES data, which is consistent with the data of the *ų*-XRF maps.

Conclusions: Future work will focus on delineating the spatial appearance of As and Pb by rescanning the same areas above the Pb LIII edge. Additional As XANES data will be collected from soil resin embedded thin sections (30μm polish) in order to avoid thickness effects of uneven samples.

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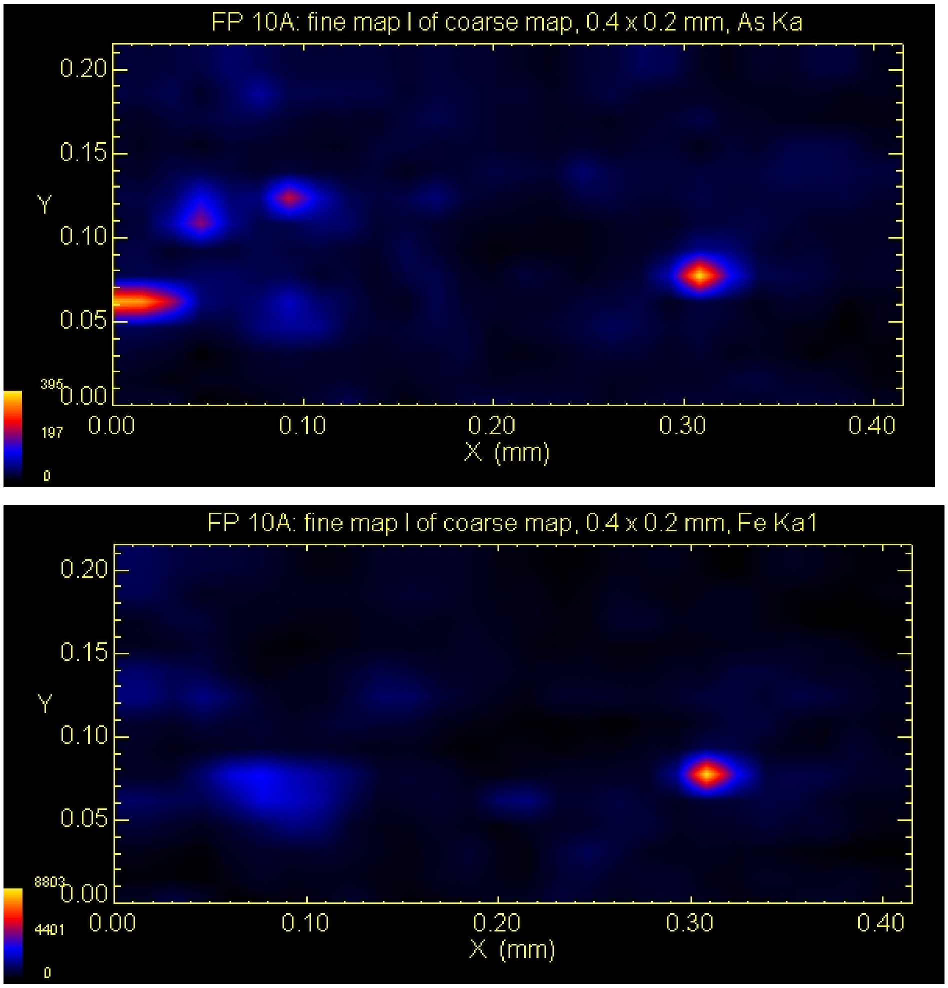

Figure 1: Micro-XRF maps of As and Fe co-occurrence in Pb-As contaminated soil.

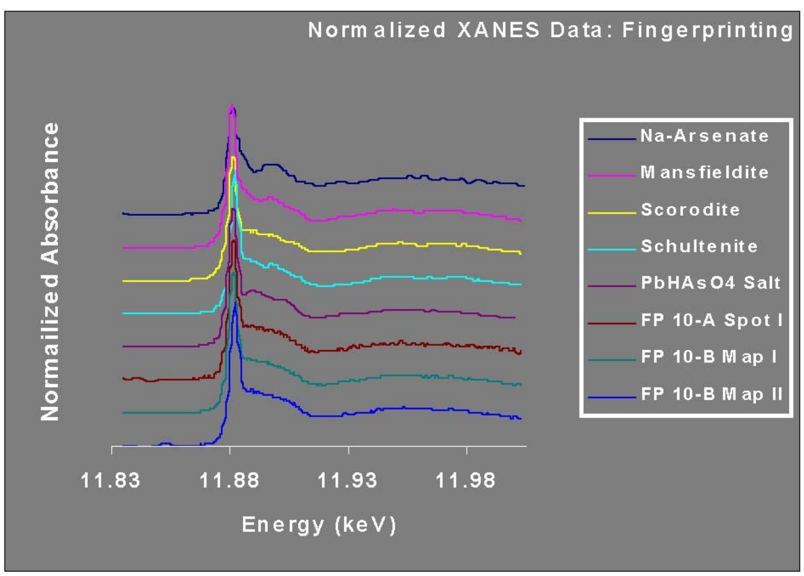

Figure 2: Normalized XANES data of selected reference minerals and salts and As hotspots on FP 10-A and 10-B.