7th ICOBTE

7th International Conference on the Biogeochemistry of Trace Elements
Uppsala, Sweden, June 15-19, 2003

CONFERENCE PROCEEDINGS

In-Situ Speciation of Arsenic Contaminated Soil Using Synchrotron Based Micro-Focused X-Ray Fluorescence and X-Ray Absorption Spectroscopy

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INTRODUCTION

Arsenic (As) contamination often occurs in areas that are considerably polluted with metal contaminants due to common mineralogical origins or anthropogenic applications involving both metals and arsenic. Little information is available about the effects of metals and metal remediation strategies on molecular scale speciation of As in soils and sediments.

Therefore, the objectives of this study were to speciate arsenic solid phases in a copper chromate arsenate (CCA) contaminated soil using synchrotron based, micro-focusing x-ray fluorescence (−SXRF) and x-ray absorption fine structure (−XAFS) spectroscopy. Complimentary desorption and sequential extraction studies were conducted to reveal the stability of arsenic in this soil.

MATERIAL AND METHODS

Contaminated soil was collected from 0-20cm (LM-A) and 20 to 40 cm (LM-B). Total elemental digests show that the As concentration was 883 mg As Kg^{-1} soil in the upper 20 cm and 251 ppm below 20 cm.

Both sequential extraction and replenishment desorption studies were conducted on LM-A and LM-B soils using the following reagents: 0.01 and 0.50 M $CaCl_2$, pH 7, 0.25 M sodium-PO_4, and 0.20 M NH_4-oxalate-0.10 M ascorbic acid. Studies were conducted in triplicate using a solid suspension concentration of 10 g L^{-1}.

Synchrotron-based spectroscopic experiments (−SXRF and −XAFS) were conducted at beamlines X-26A of the National Synchrotron Light Source (Upton, NY) and beamline 10.3.2 of the Advanced Light Source (Berkeley, CA). An average beamsize of 15x5 m was employed at both beamlines. Two dimensional −SXRF maps were collected from soils and 30 m polished thin sections to locate As hotspots and determine elemental associations. Subsequently −XAFS data were collected on selected regions at the As K-edge (11.867 keV).

RESULTS AND DISCUSSION

The −XANES experiments revealed that the oxidation state of As was +5 throughout the soil. Micro-XRF spectroscopy showed co-occurrence of As (V) with copper (Cu) and chromium (Cr), however, the most consistent spatial co-occurrence took place with zinc (Fig. 1). Correlation plots from -XRF maps showed a consistent spatial correlation of 0.9 for As-Zn, which was consistently higher than correlations for As-Cu, -Cr, -Fe or -Mn. These results are supported by both sequential extraction and desorption experiments, where the release of arsenic and zinc into solution were strongly correlated as well.

Fingerprinting −XAFS data of LM-A samples to sorption reference standards does not provide sufficient clues about the true speciation identity. While the smooth sinusoidal wave patterns of the raw $\chi(k)$ data suggest adsorption complexes, mixed copper-zinc arsenate precipitates have similar wave patterns. Micro-SXRF mapping data supports the hypotheses of mixed zinc-copper arsenate

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phases. In the LM-B soil, precipitate like phases were identified as copper-arsenate precipitates following a non-linear least squares fitting procedure using FEFF (v.7.02) generated theoretical scattering paths of orthorhombic olivenite.
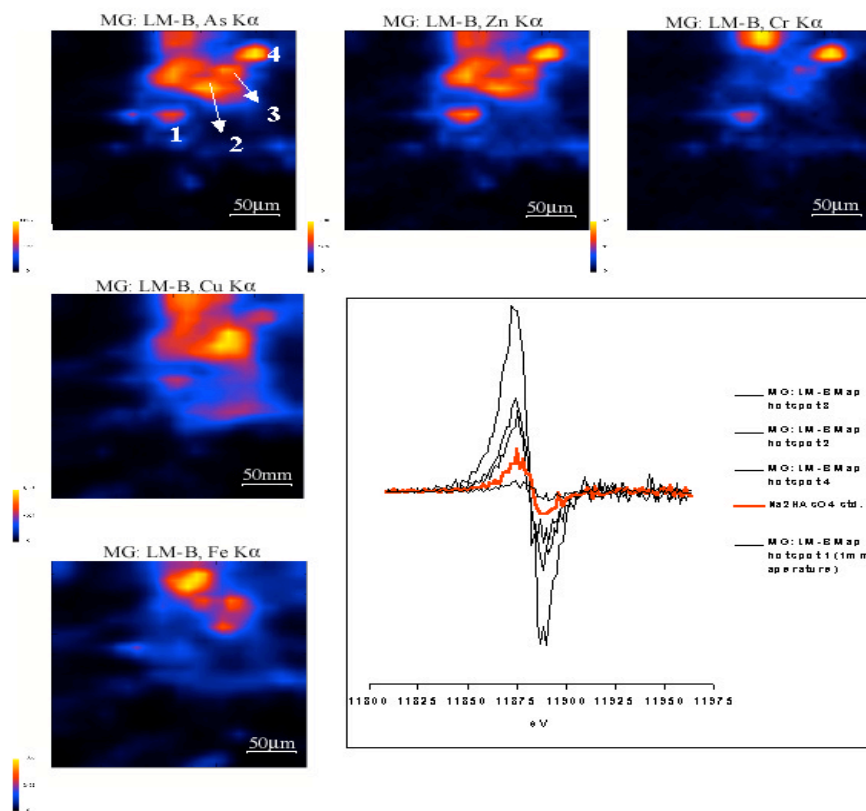

Fig. 1. ‒SXRF images collected from LM-B soil and first derivative ‒XANES analyses confirming an As 5+ oxidation state.

CONCLUSIONS
The study shows that co-contamination of metal cations significantly affects As solid phase speciation. Principal component and linear combination analyses are required to reveal the identity of As solid phases. Information gleaned from this study could prove useful in making sound decisions about environmental remediation strategies.

ACKNOWLEDGEMENTS

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