

Arsenic in the Environment - Speciation in Terrestrial Plants and Solid Material from a Biological Filtration System

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Introduction

Arsenic is best recognized as a well established human carcinogen; however, arsenic toxicity varies with its chemical form. Identification of arsenic compounds in environmental samples has been the focus of experiments conducted by the Environmental Sciences Group, at the Advanced Photon Source during the 2003 scheduling period. In particular, X-ray absorption near edge structure spectra were collected for selected vegetable species, their extraction residues, and solid materials from a biological water remediation system (Fig. 1). The water remediation system was based on a larger system built by Natural Works Remediation Corporation (Trail, B.C.) for the treatment of water contaminated with arsenic, cadmium and zinc. The vegetable work is part of an ongoing project aimed at identifying arsenic compounds present in vegetables as an indication of possible arsenic metabolic and translocation pathways. Analysis of beam damage to aqueous arsenic standards at different concentrations was also investigated.

Methods and Materials

Sample Preparation

Arsenic was supplied to plants as a solution of arsenate (reagent grade), or as arsenic contaminated soil from gold mines in Yellowknife (Canada). Plants were grown in a greenhouse at the Royal Military College (Kingston, ON). Soil samples were obtained from bioreactor cells and stored under nitrogen to maintain anaerobic conditions when necessary.

Synchrotron Analysis

All synchrotron analysis was conducted with the Pacific Northwest Consortium Collaborative Access Team (PNC-CAT), sector 20 at the Advanced Photon Source (APS), Argonne National Laboratory. X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were collected at the bending magnet (BM) beamline, while microprobe analysis was conducted with the undulator beamline. Fluorescence data was collected using a solid-state Ge(Li) detector, or an argon-filled fluorescence ionization chamber. Transmission measurements were collected using a nitrogen-filled parallel plate transmission ion chamber.

Results

Water Remediation

XANES spectra identified an arsenic-sulphur compound in the solid material of the anaerobic cell (Fig. 1A), whereas inorganic arsenate and arsenite were the main compounds in the aerobic (limestone drain) cell of the bioreactors (Fig. 1B). When solid materials were left to oxidize and analyzed again, a shift in edge energy corresponding to sample oxidation was observed.

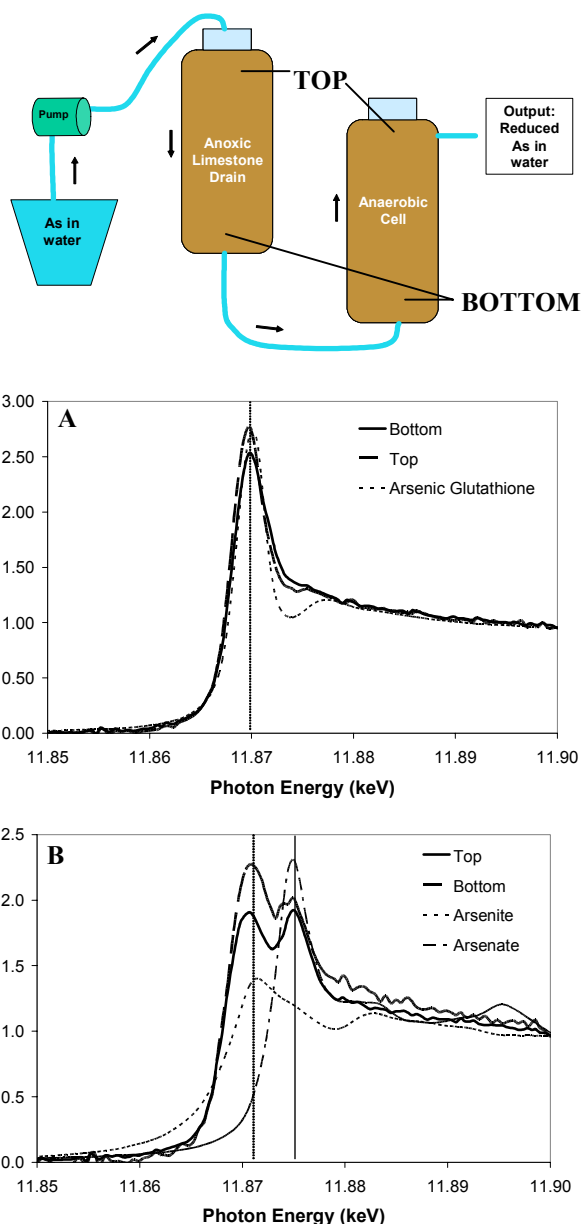


Fig. 1. (Top) Schematic of the lab scale bioreactors. Solid material was collected from the Top and Bottom of each cell. **A.** Arsenic species in solid material of anaerobic cell. Only arsenic-sulphur compounds were detected at this stage. **B.** Arsenic species in solid material from the aerobic cell. Findings may indicate reduction of arsenic.

Standards Analysis

Selected aqueous arsenic standards were tested at concentrations of 10000, 1000, 100 and 10 ppm over ~1 hour. Arsenite (100

ppm) and monomethylarsonous acid (10 ppm) spectra showed obvious shifts to higher photon energies, consistent with oxidation to arsenate and monomethylarsonic acid (MMA) respectively (MMA Fig. 2).

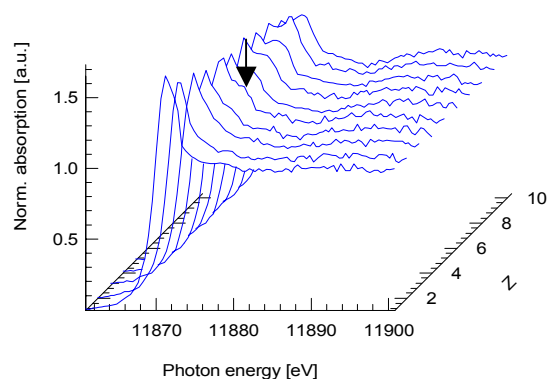


Fig. 2. Oxidation of aqueous 10 ppm monomethylarsonous acid was marked by the growth of a spectral feature (arrow) at 11.8742 keV over successive scans. This new feature has a similar white line position to that of aqueous monomethylarsonic acid. Z = scan number.

Plants and Extraction residues

An arsenic-sulphur compound was the main arsenic species identified in whole radish leaves and stem, while arsenite predominated in whole roots. Water and methanol-water extraction residue XANES spectra indicated arsenite as the major arsenic compound. XANES spectra for onion and mushroom samples indicated possible presence of arsenobetaine. Mushroom samples also contained inorganic arsenite and arsenate (Fig. 3).

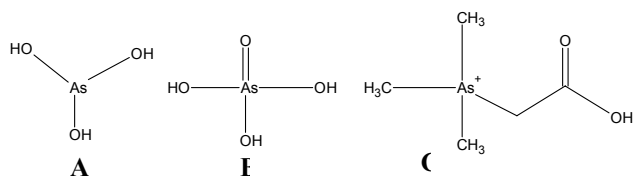


Fig. 3. Chemical structure of inorganic arsenite (A) and arsenate (B), and non-toxic, organic, arsenobetaine (C).

Discussion

Water Remediation

It has been hypothesized that sulphur reducing microorganisms in the anaerobic cell of the bioreactor produce sulphur compounds with which soluble arsenic in the water can complex. These complexes form an insoluble precipitate and arsenic is removed from the water. XANES results (Fig. 1A) support this reasoning. Traditional analytical techniques were too harsh to preserve the arsenic-sulphur compounds and extraction of the solid materials was inefficient. Arsenite and arsenate detected in the aerobic cell (Fig. 1B) may indicate reduction of arsenate to arsenic-sulphur compounds by sulphur reducing bacteria. Alternatively changes in pH and oxygen levels in the aerobic cell may be suitable for absorption of some inorganic arsenic to the biosolids of the cell.

Standards Analysis

At lower concentrations, damage attributed to total beam exposure was observed for aqueous arsenic standards. An increase in white line energy was the most commonly observed form of beam damage. This information is important to our

research since biological matrixes are predominantly water, and arsenic concentrations in samples tend to be below 100 ppm.

Plants and Extraction Residues

Results for radish samples correspond well with previous data. It appears that little transformation of the inorganic arsenic taken up from the environment is taking place. The presence of arsenobetaine in the mushrooms suggests that these fungi may be capable of converting inorganic arsenic in the environment into more complex organic arsenic compounds. Onions produce sulphur compounds and were anticipated to contain arsenic-sulphur compounds as a result. The suggestion of arsenobetaine in the samples will be further investigated. XANES spectra indicated that sample preparation and extract protocols may alter the arsenic species present in a sample. Results of more conventional arsenic species analysis (e.g. high performance liquid chromatography inductively coupled plasma mass spectroscopy) would be skewed towards the more oxidated species such as arsenite and arsenate, and under represent compounds such as those containing sulphur. X-ray absorption spectroscopy results in conjunction with ongoing studies will contribute to fundamental arsenic research on plants and fungi, and to applied research using biotechnology for the remediation of arsenic contaminated water.

Acknowledgments

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