Uptake of arsenic by *Pteris cretica*: In situ XANES study of living plants

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We are interested in understanding the uptake mechanisms and speciation of arsenic found in real environmental conditions and the implications this behavior has for the environmental remediation of arsenic. We focus on the plant-rhizosphere system, a dynamic microcosm of interdependent processes, and have chosen a known As-hyperaccumulating fern species, ***Pteris cretica***, for our study. The rhizosphere is the thin layer of soil directly in contact with the root system where the chemistry is very different from that of the bulk soil. In non-reducing environments arsenic, in the form of arsenate, passes from the bulk soil into the rhizosphere and enters the plant through the root system where it is then translocated throughout the plant by the same mechanisms that transport phosphate (an essential plant nutrient).

The results from this XANES study at X 26A and X 18B enable us to establish the oxidation state of arsenic throughout the fern as a function of time and to demonstrate where arsenic redox processes take place within the plant.

Some of our long-range research goals include resolving the coordination and oxidation state of arsenic in this system, identifying the specific types of plant cells that arsenic is stored in and understanding the effect of exudate chemistry on arsenic speciation in the rhizosphere. We also plan to look at how the presence of soil minerals such as goethite and calcite influence the effects of exudates on arsenic.

Plants and Methods

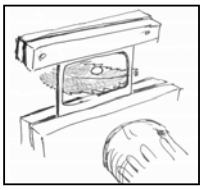
***Pteris cretica* var. Silver Ribbon**. At X26A we studied the uptake of arsenic over 24 hours. The bare roots were placed into a sample cell containing a 500 ppm Na-arsenate solution (see photos below and below left).

***P. Cretica* var. Club Foot** in the lab prior to the introduction of a 1000 ppm Na-arsenate solution to the soil. This study, performed at X18B, investigated the uptake of arsenic on a time scale ranging from 1 to 8 days after the initial As-spike. Unlike the X26A study, these ferns were allowed to remain in their pots throughout the run and only their leaves were scanned.

***P. cretica* Silver Ribbon in the hutch at X 26A.** The cell assembly allows for in situ scans of As solution only, roots in As solution, roots above the solution line and leaves (see sketch, below). The dense root mass fitted snugly between the Mylar sheets thus minimizing solution interference.

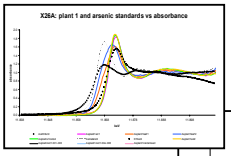
Sample cells were fabricated out of 3/8" clear acrylic. A large u-shape was cut to allow the fern to sit upright in a water-tight reservoir created using 6 µm clear Mylar and Kapton tape.

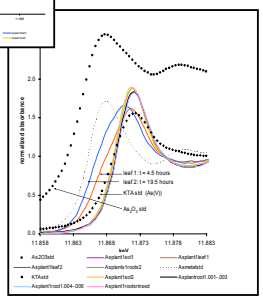
The sample cell is unattached from the stage to stand upright on the work table. Leaves (triple thickness) are held in place using a slide holder and scanned. This method of **leaf scanning** was used at X26A and at X18B.



Results

X26A





The bare root experiment conducted at X26A showed that As(V) is distributed throughout the plant within 24 hours of uptake. Spectra for the leaves indicated reduction of As(V) after 4.5 hours. Instrumental X-ray fluorescence spectrometry (Jordan Valley AR, Inc.) of the (dried) leaves showed that arsenic concentration reached approximately 2400 µg/g within 48 hours of the original arsenic spike.

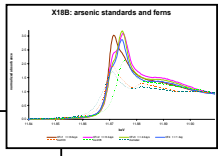
Using x-ray absorption spectroscopy we investigated the oxidation state and distribution of arsenic in *P. cretica* at X26A and at X18B. XANES spectra for As(III), As(V), and As metal standards were collected and compared to the plant data for each run.

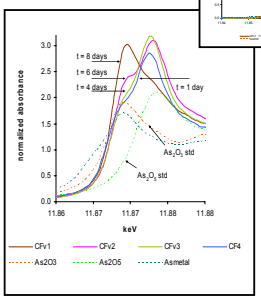
The redox state of As was determined by evaluating the position of the absorption edge relative to the standards. The plants that had the shortest period of As-uptake prior to scanning have spectra that most closely resemble that of the As(V) standard with respect to edge position as well as the general spectral shape. A shift of the plant spectra to lower energy (towards the As(III) spectra) indicated the arsenic was being reduced. The development of an As(III) shoulder in the plant spectra as reduction progressed is clearly shown by the XANES collected at X18B (right).

Arsenic was shown to be distributed throughout the ferns.

This study confirms the usefulness of *P. cretica* as a potential environmental remediator of arsenic. Future work will attempt to identify electron donors promoting arsenic reduction in this system, identify cells used to store As, and characterize As-complexation in the leaves.

X18B





The soil experiment conducted at X18B showed a significant amount of As(V) was reduced to As(III) over 8 days.

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