Cattail Root Plaque Retention of Arsenic

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Introduction

Human exposure to arsenic in the environment may be reduced by mechanisms that sequester arsenic from the groundwater into the solid phase, which can limit its presence in drinking water or its transport from a contaminated site. Wetlands are recognized for their ability to sequester contaminants and have been constructed in recent years to filter waste streams [1]. Making a determination of the mechanisms that retain arsenic in wetlands was previously limited by the available experimental techniques. Our understanding of the biogeochemical processes promoting arsenic sequestration has been significantly advanced by the application of x-ray absorption spectroscopy, including x-ray fluorescence (XRF) microtomography, coupled with tested, targeted chemical extractions.

Wetland plants form dense root networks in upper wetland sediments and, under flooded conditions, pump oxygen to their roots for respiration [2]. Oxygen may be exuded from the roots and can react with dissolved ferrous iron to form an iron-rich plaque on the root surfaces [3]. The influence of plaque formation on arsenic cycling may be significant because of the high adsorptive affinity of arsenic for iron hydroxides. Iron plaque formation on wetland plant roots was confirmed by various methods, including scanning electron microscopy (SEM) [3] and XRF microtomography [4]. Arsenic concentrations, however, were below instrumental detection limits to image the distribution in the plaque by using SEM or electron microprobe [5].

To investigate whether arsenic is sequestered in wetland plant root plaques and/or inside the roots, we applied XRF microtomography to image the distribution of arsenic in a root cross section. We compared the distribution of arsenic with iron in the plaque to determine if the elements were correlated on a small (5-µm) spatial scale. In addition, we examined the speciation of arsenic in the plaque [As(III) vs. As(V)], which is important because of the higher toxicity and mobility of the As(III) species.

Methods and Materials

Typha latifolia (cattail) roots were collected from the Wells G & H wetland, Woburn, MA. The 16-ha Superfund site wetland contains approximately 10 tons of arsenic within the sediment root zone. Roots were separated from the soil within a nitrogen-purged glove bag to prevent oxidation of ferrous iron on the roots, which may be induced by exposure of the roots to oxygen. Roots for total fluorescence analysis were freeze-dried to remove the water. In early tests, we found that wet roots dried during the analysis time and did not maintain structural integrity; elemental map reconstructions require a stationary sample around the vertical axis. For arsenic oxidation state mapping, we impregnated the roots with oil to prevent any potential oxidation that might occur during freeze-drying.

Elemental distributions were determined through a cross-sectional root slice (without physically cutting the root) at undulator beamline 13-ID-C at the APS. XRF data were collected simultaneously for several elements by using a solid-state germanium detector. Roots were mounted on a computer-controlled platform, translated at 5- to 10-µm steps through the stationary 2- to 3-µm pencil beam operated in fluorescence mode, and rotated by 5º around the vertical axis, followed by repeated translation and rotation for a total of 180º root rotation. Arsenic oxidation state maps were produced by measuring fluorescence intensities at the As(III) and As(V) white line energies (E_3 and E_5, respectively), at an energy above the edge for total As (E_T), and at an energy below the edge for background (E_0) (Fig. 1).

To investigate the mechanisms retaining arsenic in the plaque, root surfaces were extracted according to the

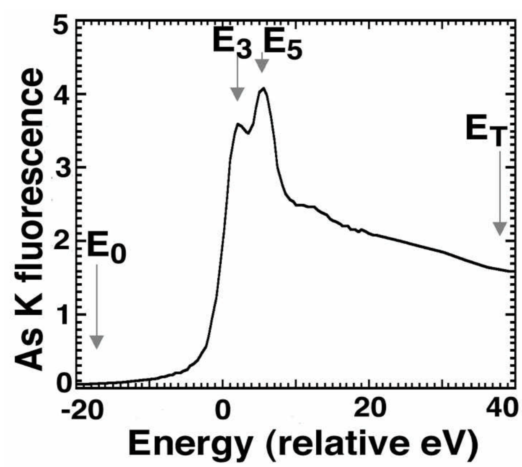

FIG. 1. Energies selected for oxidation state maps.

sequential extraction procedure of Keon et al. [6]. The extraction was previously standard-tested by using known arsenic phases, including adsorbed arsenic and various coprecipitated arsenic phases. Extractant solutions were measured for arsenic and iron content by graphite furnace atomic absorption spectroscopy.

Results

SEM images of *T. latifolia* roots from the Wells G & H wetland showed high concentrations of iron on root surfaces, but arsenic was below the SEM detection limits of approximately 0.1% (Fig. 2).

XRF microtomograms demonstrated that arsenic and iron are distributed in a continuous ring around the outer edge of the roots (Fig. 3). The iron plaque ranged from 15 to 30 μm in thickness for roots between 100 and 500 μm in diameter. Arsenic and iron in the root plaques were highly correlated at a scale of 5 μm (R^2 of >0.95). In contrast, we found that co-contaminants at the Wells G & H wetland site, including lead, copper, and zinc, were not correlated with iron.

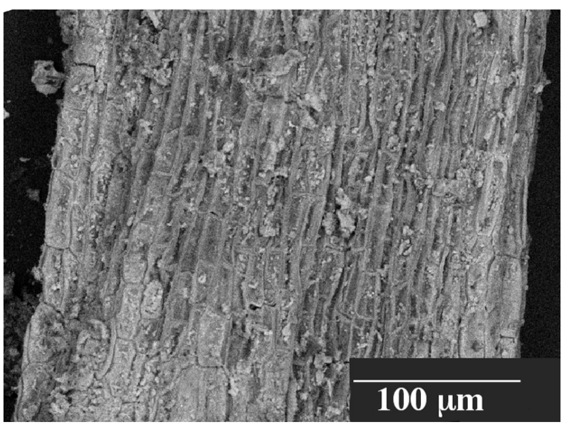

FIG. 2. Backscatter SEM image of the root surface depicted in the tomograms.

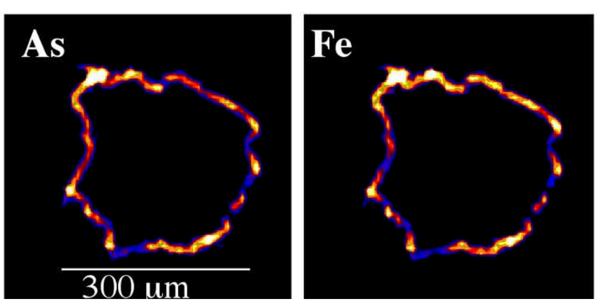

FIG. 3. XRF microtomograms of arsenic and iron distribution in a 2-D slice through a T. latifolia root, showing that both elements co-map on the outer edge of the root.

Chemical extractions of the plaque showed that more than 90% of the arsenic was strongly adsorbed (i.e., competitively desorbed by phosphate solution). Iron phases in the plaque were found to be likely ferrihydrite or $FeCO_3$ (i.e., 1N HCl-extractable during a short 1-h extraction).

Oxidation state mapping of the arsenic distribution in a second root plaque showed a fairly heterogeneous mixture of As(III) and As(V) (Fig. 4, squared area). As(III) appears to be slightly more likely to be distributed in the interior of the plaque (circled region).

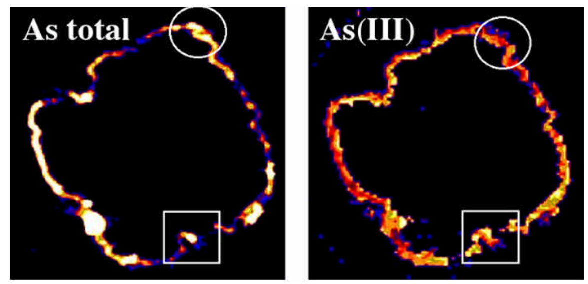

FIG. 4. Oxidation state maps of As(III) and total As within the root plaque of a second root.

Discussion

In the Wells G & H wetland, arsenic in the root plaque is highly correlated with iron and confined to a ring around the outer edge of the root. Arsenic-to-iron ratios ranged from 3 to 120 mmol arsenic/mol Fe, determined by both XRF microtomography and chemical extractions. The combination of the molar ratios and the finding that the plaque arsenic was mostly phosphate-extractable support the hypothesis that As is sorbed to amorphous Fe phases such as ferrihydrite or possibly iron carbonate. Further analysis of Fe speciation in the plaque may elucidate the character of the Fe phase.

For the first time, the feasibility of oxidation state mapping by using XRF microtomography was demonstrated for plant roots. A mixture of As(III) and As(V) phases was observed in all roots tested. Similarly, the pore water contains a mixture of As species. These findings support the hypothesis that pore-water arsenic is drawn to the roots and that both species are sequestered in the plaque. The possibility that As(III) may be located preferentially in the interior of the root (indicated in Fig. 4, circled area) needs to be explored further by the analysis of additional roots.

Mass balance calculations of arsenic sequestered in the root plaque (from arsenic content in the plaque and estimated plaque volume per cm^3 of sediment) revealed that the plaque sequesters a significant proportion of aqueous pore-water arsenic. Release of the plaque arsenic into the pore water would increase pore-water arsenic concentrations by a factor of 1000. In conclusion, *T. latifolia* root plaques appear to play an important role in sequestering aqueous arsenic in contaminated wetlands.

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