



## **Effect of dissimilatory iron and sulfate reduction on Arsenic dynamics in the wetland rhizosphere and its bioaccumulation in plants**

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Arsenic (As) pollution in water soil and sediments is of worldwide concern due to its ecological toxicity and chronic effects on human health. Wetlands are at the interface between ground and surface waters and because of their unique biogeochemical dynamics could be promising location for arsenic immobilization. However, the nature of biogeochemical reactions of As in wetlands are complex and not well understood. The dynamics of As in wetland sediments are closely linked to the redox cycling of Fe and S, both of which are affected by water-table fluctuations and wetland plants activity that are typical in such environments. Little is not known about redox cycling of Fe or S and their effects on As speciation, biogeochemical dynamics, and bioaccumulation in the wetland rhizosphere and plants.

To gain further insights into these processes, twelve mesocosms were set up and planted with wetland plants (*Scirpus actus*), six were submerged in a tray (reactor) with  $\sim 170$  mM  $\text{SO}_4^{2-}$  and six in a tray with  $\sim 350$   $\mu\text{M}$   $\text{SO}_4^{2-}$  and two levels of ferrihydrite in the soil for each  $\text{SO}_4^{2-}$  treatment. Each mesocosm was sealed and the only contact with the solution in the reactor was via the surface of the mesocosm. The mesocosms were run for 1.5 months to establish the plants, after which  $50\mu\text{M}$   $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  was added to the reactors. Water in the reactors was constantly recirculated to make the solution homogeneous. The reactors were run for 4 months and monitored regularly for dissolved species, and were then dismantled.

Results show that the presence of plants, high Fe, and high  $\text{SO}_4^{2-}$  levels enhanced As sequestration in the soil. We hypothesize that the reason for this compounding effect is that plants release easily biodegradable organic carbon, which is used by microorganism to reduce ferrihydrite and  $\text{SO}_4^{2-}$  to generate FeS or FeS<sub>2</sub>. More As is then sequestered via sorption or co-precipitation on FeS or FeS<sub>2</sub>. Analysis of As in plant tissue showed that As uptake by *Scirpus actus* was mainly controlled by  $\text{SO}_4^{2-}$  rather than Fe levels. When dissolved  $\text{SO}_4^{2-}$  levels decreased from  $\sim 170$  mM to  $\sim 350$   $\mu\text{M}$ , As concentrations in plant tissue increased by 97%, whereas no significant changes in plant As levels were seen for varying Fe concentrations in the soil.

The As distribution in plant leaves and roots after 30 days of exposure to As was analyzed via Synchrotron X-ray fluorescence analyses. Compared with controls (no As addition), the uptake of As by plants was distributed along leaves veins for all plants exposed to As. The distribution of As in roots was correlated with the distribution of Fe in the roots, rather than with Ca or Zn, indicating that As may be co-distributed with Fe in plants.