Fate of Uranium During Transport Across the Groundwater-Surface Water Interface

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Discharge of contaminated groundwater to surface waters is of concern at many DOE facilities. Essentially all surface or subsurface contaminants will move vertically through a vadose zone to an underlying aquifer and then laterally until it reaches some riparian zone or wetland. For example, at F-Area and TNX-Area on the Savannah River Site, contaminated groundwater, including uranium, is already discharging into natural wetlands. It is at this interface where contaminants come into contact with the biosphere. These wetlands exist in humid as well as arid regions. Furthermore, the numerous sharp biogeochemical transitions occurring in wetlands have profound effects on the ultimate fate of redox-sensitive trace metals and radionuclides, including uranium.

The goal of this research is to provide new insights on how plant-induced alterations to the sediment biogeochemical processes affect the key uranium reducing microorganisms, the uranium reduction, its spatial distribution, the speciation of the immobilized uranium, and its long-term stability. For this purpose we have formulated the following three **hypotheses**. (1) U(VI) discharged from ground- to surface-waters can be immobilized effectively as U(IV) in the sediments at the groundwater-surface water interface. The electron donor required to stimulate the microorganisms capable of reducing U(VI) is provided by wetland plants via their root exudates and root turnover. (2) Oxygen released into the sediments by plants reoxidizes Fe(II), forming iron oxy(hydroxi)des, which provide the bioavailable Fe(III) for long-term bacterial iron-reducing activity, which is key for a sustained biological uranium reduction. (3) Because wetland sediments are anaerobic and wetlands are usually nitrogen limiting, uranium immobilized as U(IV), which is readily oxidized in the presence of nitrates, will remain stable in the sediments for extended time periods.

To test these hypotheses we initiated a series of greenhouse **mesocosm studies** in which we will simulate the discharge of uranium contaminated groundwater into surface water through vegetated and non-vegetated sediments. These mesocosm studies, which will give information regarding macroscopic-scale processes and kinetics, will be augmented with laboratory batch studies to isolate the effect of specific variables. This characterization will be to determine the role the root-induced biogeochemical dynamics have on Fe speciation (to be determined via micro-XRD and Mössbauer analyses), microbiologic activities (^{13}C stable isotope pulse chase experiments coupled with ^{13}C phospholipid fatty acid analysis and pyrosequencing), and their role in controlling U speciation/oxidation states (via X-ray Absorption and X-ray fluorescence Spectroscopy) and U partitioning between the solid and aqueous phases. Spatial distribution of these characterizations and processes from the root surface to the bulk sediment will be quantified to gain detailed new insights into these biogeochemical processes and their overall impact onto the dynamics of uranium at the groundwater-surface water interface.

The project has just been initiated and we will show initial results of the microcosm operation, specifically the microbial community differences, including *Geobacter sp.* numbers as we move away from the root surface into the rhizosphere and into sediments where root growth has been excluded. Characterization of three U-contaminated wetland sediments from the SRS have shown that the U is only slightly more preferentially associated (1.5x) with the fine particle fraction (<2- μm or <0.5-μm), whereas Th(IV) was strongly concentrated (29x) in the finer particle size fraction. A sequential extraction of these sediments revealed that ~50% of the U in these heavily contaminated sediments was organically bound (sodium pyrophosphate extractable),7% was either associated with amorphous or crystalline Fe-oxides (extractable with ammonium oxalate or dithionite extractable), and another ~25% was exchangeable (acetic acid exchangeable). Uranium extractions were not similar to Th(IV) extractions, suggesting that some of the U may exist in the +6 oxidation state. Together these data indicates that: 1) the soil organic carbon is responsible for most of the sequestration of uranium in the wetland, and 2) a vast majority of the uranium in these wetland sediments may be in a labile state associated with organic matter, exchangeable fraction, and iron oxides in this dynamic chemical system.