Organic Matter Sources in the Speciation and Mobilization of Pu in the Subsurface Environment of the Rocky Flats Site

Nicole DiDonato (ndidonat@odu.edu) - Old Dominion University, Dr. Peter Santschi (PI), Dr. Patrick Hatcher, ODU; Dr. Chen Xu, TAMUG; Dr. Kathleen A. Schwehr, TAMUG (Co-PIs).

Plutonium from contaminated soils at the Rocky Flats Environmental Technology Site (RFETS) was found to be concentrated in an organic fraction containing degradation products of the biopolymer cutin, as well as hydroxamate and hydrophilic moieties indicative of polysaccharides [1]. Traditionally found associated with inorganics, this represents a pivotal advancement in understanding Pu transport and biogeochemistry. Cutin biopolymers contain esters that can react with amines to incorporate nitrogen species [2]. This is one mechanism by which hydroxamate siderophores also present in soils at RFETS may be incorporated into organic matter, thus accounting for its high affinity for Pu.

The objective of this research was to isolate cutin from samples of Western wheatgrass (Agropyron Smithii), a dominant species of vegetation and likely contributor to soil organic matter at RFETS. The chemical isolation procedure [3] was modified and optimized to remove recalcitrant cellulose and lignin structures prevalent in grasses. Solid state 13C CPMAS NMR and two-dimensional HRMAS HSQC, TOCSY and COSY experiments were utilized to identify and characterize the isolated polymer.

Research results of the isolated material indicate the presence of crystalline and amorphous aliphatic long-chain polymethylenes containing esters, fatty acids, and primary and mid-chain hydroxy acids characteristic of cutin [3]. Also evident are residual carbohydrate/cellulosic material and aromatic groups in low but detectable quantities, reminiscent of the IEF extract containing Pu [1]. Thus it is likely that this biopolymer has contributed to the organic fraction of soil responsible for accumulating Pu and rendering it more mobile.

The interaction of cutin with deferoxamine, a tri-hydroxamate siderophore indicative of siderophores likely present in RFETS soils, and subsequent interactions with metals such as Pu and Fe are under investigation. These experiments along with analytical techniques such as 13C NMR, HRMAS, FTIR, etc., will further identify the molecular structure of wheatgrass cutin and clarify the role cutin may play in interactions with microbial siderophores and sequestering metals such as Fe and Pu in soils. This work fills an important gap linking the distinct sources of organic material in soils to their specific role in controlling the biogeochemical cycling of metals.

References:

