Plutonium Immobilization and Mobilization by Soil Organic Matter

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Background: The human and environmental risks associated with Pu disposal, remediation, and nuclear accidents scenarios stems mainly from the very long half-lives of several of its isotopes. The SRS, holding one-third of the nation's Pu inventory, has a long-term stewardship commitment to investigation of Pu behavior in the groundwater and downgradient vast wetlands.

Pu is believed to be essentially immobile due to its low solubility and high particle reactivity to mineral phase or natural organic matter (NOM). For example, in sediments collected from a region of SRS, close to a wetland and a groundwater plume, ^{239,240}Pu concentrations suggest immobilization by NOM compounds, as Pu correlate with NOM contents. Micro-SXRF data indicate, however, that Pu does not correlate with Fe. However, previous studies reported Pu can be transported several kilometers in surface water systems, in the form of a colloidal organic matter carrier, through wind/water interactions. The role of NOM in both immobilizing or re-mobilizing Pu thus has been demonstrated. Our results indicate that more Pu (IV) than (V) was bound to soil colloidal organic matter (COM), amended at far-field concentrations. Contrary to expectations, the presence of NOM in the F-Area soil did not enhance Pu fixation to the organic-rich soil, when compared to the organic-poor soil or the mineral phase from the same soil source, due to the formation of COM-bound Pu. Most importantly, Pu uptake by organic-rich soil decreased with increasing pH because more NOM in the colloidal size desorbed from the particulate fraction at elevated pH, resulting in greater amounts of Pu associated with the COM fraction. This is in contrast to previous observations with low-NOM sediments or minerals, which showed increased Pu uptake with increasing pH levels. This demonstrates that despite Pu immobilization by NOM, COM can convert Pu into a more mobile form.

Methods: We have determined ambient Pu concentrations and isotopic ratios with ICP-MS and alpha spectrometry, in samples collected from both SRS and Fukushima Prefecture [1-3]

Results: Sediment Pu concentrations in the SRS F-Area wetland were correlated to total organic carbon and total nitrogen contents and even more strongly to hydroxamate siderophore (HS) concentrations. The HS were detected in the particulate or colloidal phases of the sediments but not in the low molecular fractions (< 1000 Da). Macromolecules which scavenged the majority of the potentially mobile Pu were further separated from the bulk mobile organic matter fraction ("water extract") via isoelectric focusing experiment (IEF). An ESI FTICR-MS spectral comparison of the IEF extract and a siderophore standard (desferrioxamine; DFO) suggested the presence of HS functionalities in the IEF extract.

The cuticle material from Western wheatgrass (*Agropythi Smithii*), one of the dominant vegetation species at the RFETS, was extracted, and carbohydrates removed from the crude cuticle extract. Oxidation and depolymerization experiments of cutin, incoporation of carbohydrates, siderophore compounds, as well as the chelation of Fe(III) (as a surrogate of

Pu(IV)) during a simulated humification process, were assessed by ^{13}C NMR, HRMAS, ATR-FTIR, etc.).

This study suggests that while HS are a very minor component in the sediment particulate/colloidal fractions, their concentrations greatly exceed those of ambient Pu, and HS may play an especially important role in Pu immobilization and re-mobilization in soils from different climatic regions, e.g., from grasslands in Colorado, wetlands in South Carolina, and paddy, urban, deciduous forest and coniferous forest soils from Japan.

References:

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