Plutonium Immobilization and Mobilization by Soil Organic Matter

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Pu is believed to be essentially immobile in groundwater due to its low solubility and high particle reactivity to mineral phase or natural organic matter (NOM). 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. For example, in sediments collected from SRS, close to a wetland and a groundwater plume, ^{239,240}Pu concentrations are more closely correlated with organic nitrogen content than the bulk organic carbon content, suggesting ^{239,240}Pu immobilization by nitrogen-containing organic compounds. More intriguingly, hydroxamate siderophores, which are a strong iron-complexing ligand produced by microbes, are shown to be one class of the nitrogen-containing compounds (0.15-5.51% of total organic nitrogen) and are thought to be responsible for scavenging and fixing Pu in the sediment, due to its high binding constants. Additional supporting evidence that nitrogen-containing organic compounds control Pu transport was obtained from surface soil cores from three distinct soil types: paddy soil, deciduous soil and coniferous soil in the Fukushima Prefecture after the FDNPP accident. Although Pu was believed to be mostly contributed by global fallout, atmospheric fallout from 1963-1979, and atomic bomb events prior to the FDNPP accident, we found that Pu was strongly associated with organic nitrogen in these sediments, too. Electrospray Ionization-Fourier Transform Ion Cyclotron Mass Spectrometry (ESI-FTICRMS) was applied to investigate the Pu enriched fraction, which was collected from a surface sediment soil of the SRS by several separation and purification steps: 1) soil leaching by artificial groundwater; 2) filtration and ultrafiltration to obtain the 0.45 μm to 1 kDa fraction; 3) isoelectric focusing electrophoresis (IEF) experiment to obtain the Pu-enriched fraction; 4) ultrafiltration to rinse off the detergent and buffer. Pu-enriched macromolecules mostly belong to the class of lipids, but are also contributed by lignin, proteins, unsaturated hydrocarbons and condensed hydrocarbons. Formulas of the nitrogen-containing compounds overlap with the bulk formulas. A comparison of the mass spectra of DFO-B and Pu-enriched macromolecules confirm the presence of siderophores in this Pu organic carrier phase. It is thus very likely that hydroxamate siderophores, with a molecule weight of less than 1 kDa, together with other unknown nitrogen-containing compounds, were once produced by microbes and then incorporated into a large macromolecule. This provides a novel mechanism for surface Pu migration in organic-rich terrestrial systems.