NAME: Peter H. Santschi
ORGANIZATION: Texas A&M University - Galveston
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Plutonium Immobilization and Re-mobilization by Soil Mineral-Organic Matter Matrix Compounds

ABSTRACT: 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 [2,3]. The role of NOM in both immobilizing or re-mobilizing Pu thus has been demonstrated. It was found that partitioning coefficients (K_d) of intact humic acids (HAs) were sigificantly higher than those when HA was treated with HF, due to a lower number of chelating sites for Pu in the HF-treated HAs, or due to hydrophobicity differences between the two types of HAs. K_ds of Pu (IV) with HAs were higher at low pH (4.4) than those at high pH (7.1), in contrast to the observation of Pu sorption to most mineral phases [4], possibly caused by the increased solubility of HA under more alkaline conditions. Though the colloidal fraction of HAs (>1kDa MWCO) only accounts for a minor fraction of total OC (<5%) at pH 4.4, Pu binding to HAs accounts for 61-83% of the total added Pu, indicating that colloidal organic matter is the mobile Pu carrier in the wetland area. Lastly, ^{239,240}Pu concentrations were found to be positively correlated to particulate hydroxamate and nitrogen contents, demonstrating Pu binding to siderophores, a NOM compound. Additional research involves the extraction and synthesis of the NOM precursor of the organic Pu carrier. In a previous study, almost all of the mobile ^{239,240}Pu in a soil sampled from near the contaminated 903 Pad in the Rocky Flats Environmental Technology Site (RFETS) was found to be associated with a macromolecule having cutin degradation products as the backbone, crosslinked to some hydrophilic moeties such as polysaccharides (to increase its solubility and thus mobility), hydroxamate (one type of siderophore compounds), and amide functionalities (both to chelate iron and Pu) [3]. To help understand Pu interactions with cutin and siderophore degradation products, a modified method [5] was used to extract the cuticle material from Western wheatgrass (*Agropythi Smithii*), one of the dominant vegetation species at the RFETS. The crude cuticle extract contains a significant portion of residual carbohydrates and amide functionalities. This cutin material was further purified to remove carbohydrates. Oxidation experiments were carried out to investigate the depolymerization of cutin, incoporation of carbohydrates, siderophore compounds, as well as the chelation of iron(III) (as a surrogate of Pu(IV)) during a simulated humification process. Finally, using advanced analytical tools to quantify and identify NOM moities (^{13}C NMR, HRMAS, ATR-FTIR, etc.), this material was compared with the naturally-occuring organic colloidal Pu carrier [3] to unravel the history of the molecular basis for the Pu vector in the enviroment.. **References:** [1] Kaplan et al. (2007), *ES&T* 41, 7417-7423. [2] Santschi et al. *ES&T* 36, 3711-3719. (2002). [3] Xu et al. (2008) *ES&T* 42, 8211-8217. [4] Kaplan et al. (2006), *ES&T* 40, 5937-5942. [5] Deshmukh et al. (2003) *Phytochemistry* 64, 1163-1170.