Hydroxamate Siderophores in soil mineral-organic matter matrix Responsible for Binding ^{239,240}Pu in the Far-field of the Savannah River Site, USA

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Siderophores are low molecular weight organic ligands that have extremely high affinities for Fe^{3+} and are excreted by plants and microbes to acquire iron [1]. In a DOE contaminated soil [2], Pu(IV), that has a similar charge-to-ionic size ratio as Fe(III), was previously demonstrated to be bound by hydroxamates that were embeded in cutin degradation products cross-linked to hydrophilic moeties (e.g., polysaccharides). In the far-field of the Savannah River Site (SRS), USA, not only was Pu in the wetland surface soil found to be associated with natural organic matter (NOM) [3], but it was also closely related to hydroxamate siderophores present as a minor fraction (0.002-1.4%) in the bulk NOM pool. These hydroxamate siderophore moieties can be easily overlooked due to detection difficulties [4]. Thus, diluted HF (10%) was used to break the mineral-NOM matrix, making hydroxamate accessible to the hydrolysis solution. In addition, a control blank was subtracted to correct for the interference by humics. In SRS soils, hydroxamates were found to be the major type of siderophores, and mostly found in soil particles rather than in solution during a soil-groundwater re-suspension experiment. From the observation that particle-bound hydroxamate concentrations increase with depth in soil profiles, it appears that hydroxamates are preferentially preserved during early diagenesis. Attempts to incorporate hydroxamates into degraded cutin polymers and then use multi-dimensional NMR techniques to characterize their structure are currently underway, with the aim to confirm the pathway of forming cutin-bound hydroxamate metal complexes capable of immobilizing Pu in soils.

[1] Neu (2000), *Chemical Interactions of Actinides in the Environment*, **26**, 416-417. [2] Xu *et al* (2008) *ES&T* **42**, 8211-8217. [3] Xu *et al* (2014) *ES&T* **48,** 3186-3295 [4] Gillam, *Anal. Chem.* **53**, 841-844.