The Role of Natural Organic Matter in Immobilizing or Re-mobilizing Plutonium in the Far Field of the Savannah River Site, USA

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Plutonium (Pu) contamination of soils or groundwater can be a serious problem at DOE sites. Pu is an element with a complex chemistry, exhibiting a number of oxidation states in aquatic environments, predominantly Pu(IV) and Pu(V). In surface and subsurface waters, the prevailing Pu oxidation state depends on the abundance of natural organic matter (NOM) and selected minerals. NOM reducing moieties can significantly modify the mobility of Pu in the environment by producing colloidal organic carriers that strongly bind Pu, mostly as Pu(IV). **Objectives:** *Objective 1:* Build on our successful characterization of the chemical composition of organo-Pu species in water leachates from the remediated RFETS site by using a similar approach on other soils or aquifer sediments from different Pu-contaminated DOE sites. These Pu-associated ambient colloidal organic leachates will then be compared to those that have formed over time when a Pu tracer was added to the same soils, and will be used for transport studies. *Objective 2:* Determine the biogeochemical factors that give mobility and/or immobility to the colloidal organic carrier molecule. This requires a full molecular level characterization of the chemical composition of strongly Pu-binding biopolymers in NOM extracted from laboratory incubation, leaching and column studies with these soils. *Objective 3:* Determine thermodynamic stability constants of Pu to the well-characterized Pu-carrying NOM compounds isolated from Pu contaminated soils. **Hypotheses:** *H1:* Mobile organic Pu species from Pu contaminated soils contain biomarker compounds that can be used to predict the future spread of Pu contamination as well as Pu bioavailability. *H2:* Amphipilic EPS molecules of moderate molecular weight (e.g., 5-50 kDa) containing reducing moieties (e.g., hydroquinones, ferredoxins, or flavodoxins) with clustered ligand groups for Fe(III)-binding are most effective in immobilizing organo-Pu species that sorb to sediment particles, while colloids of ≤105 kDa molecular mass are potentially mobile in groundwater. *H3:* Binding constants of Pu to well characterized Pu-carrying NOM compounds isolated from Pu contaminated soils depend on applied Pu concentrations due to the well-known surface site heterogeneity effect. **Experimental design:** The objectives of this proposal will be accomplished through collaborative research at TAMUG and ODU, as well as researchers from national laboratories. **The potential benefits** of the project to DOE are a better understanding of the role and mobility of different organic bio- and geopolymeric Pu vectors that will greatly advance science in general, and in particular, biogeochemistry of Pu at low, environmental levels. **Preliminary Results**: In the present study, SRS sediment cores collected from a reservoir lake, which was used as part of a cooling water loop for two production reactors during the period 1961 to 1964, is analyzed for elemental composition and plutonium content. A significant positive correlation is shown between NOM content and Pu concentration. Humic acid obtained from these sediments extracted following the IHSS standard method is prepared in different ways, and Kds of Pu to the humic acid fraction are calculated and compared. Pu bound NOM is further separated and purified using isoelectric focusing method [Xu et al., 2008. ES&T 42, 8211-8217]. Composition of the Pu enriched organic fraction is determined by elemental analysis, FT-IR, NMR, and FT-ICR-MS.