Uranium speciation and dynamics in contaminated wetland sediments

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Several sites in the United States and around the world have significant amounts of depleted uranium (^{238}U) as a legacy contaminant from Cold War activities and nuclear fuel production. Predicting the transport and dispersal of these stocks is of paramount importance to public safety—in order to inform policy decisions reactive transport models must adequately account for U transformations in complex natural systems. This necessitates a molecular-level understanding of the interfacial and redox chemistry of U in the presence of minerals, bacteria, and dissolved ligands.

In this work we examined the speciation and transformations of U in sediments from a contaminated field site (the Tims Branch wetland at the Savannah River Site). Sediment cores taken near a stream at the site consisted of organic-rich layers (OL) overlaying mineral layers (ML). The OL was enriched in U (44.5±17.1 ppm) relative to the ML (6.38±2.19 ppm). Using synchrotron x-ray spectroscopy (Fe K-edge XANES) we observed 13% - 30% Fe^{II}/Fe_{total} in the saturated sediments, indicating the presence of reducing conditions. U L_{III}-edge XANES and EXAFS spectroscopy indicated that >95% of U associated with the saturated sediment was non-uraninite U^{IV}. Comparisons of the EXAFS spectra to those of U^{IV} species in defined laboratory systems (biogenic nanoparticulate uraninite, mononuclear U^{IV} adsorbed to mineral and bacterial surfaces) suggest that ≡TiO sites in the sediment minerals may be responsible for U^{IV} complexation. Alternating oxic/anoxic incubations of the sediments amended with glucose demonstrated a facile and reversible transition between adsorbed U^{VI} and mononuclear U^{IV} species. The observed valence transitions of sediment-associated U in response to redox variations that are typical of wetland environments suggest that the lability of both U^{VI} and U^{IV} species must be considered when modeling U transport in wetlands. The observed non-uraninite U^{IV} species present a particular challenge in that respect, as very limited thermodynamic and kinetic data are avaialble for inclusion of such species in reactive transport models.