

## Partitioning of Uranyl Between Ferrihydrite and Humic Substances at Acidic and Circum-neutral pH

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The effect of reference humic and fulvic substances on the sorption of uranyl on 2-line ferrihydrite (Fh), a common naturally occurring nano-Fe(III)-hydroxide, was examined. Uranyl was reacted with Fh at pH 4.6 and 7.0 in the presence and absence of Elliott Soil Humic Acid (ESHA) or Suwanee River Fulvic Acid (SRFA). The following three size fractions were considered: (1)  $\geq 0.2 \mu\text{m}$  (Fh–NOM aggregates), (2) 0.02 to  $0.2 \mu\text{m}$  (dispersed Fh nanoparticles and NOM macromolecules), and (3)  $< 0.02 \mu\text{m}$  (dissolved). Partitioning of uranyl between Fh and NOM was determined in size fraction (1). The presence of ESHA in the uranyl–Fh–NOM ternary system at pH 4.6 enhances uranyl uptake more than the presence of SRFA. In contrast, neither form of NOM affects uranyl sorption at pH 7.0 over most of the NOM concentration range examined (0–500 ppm); at the highest NOM concentrations (500–955 ppm) uranyl uptake in the aggregates is slightly inhibited at pH 7.0, likely due the dispersion of Fh aggregates. X-ray absorption spectroscopy at the U  $L_{\text{III}}$ -edge was used to characterize molecular-level changes in uranyl complexation as a result of sorption to the Fh–NOM aggregates. At pH 7.0 the majority of uranyl was directly sorbed to Fh and only a small proportion of uranyl was complexed to NOM over the whole range of concentrations studied. However, when NOM concentration was increased at pH 4.6, the proportion of uranyl–NOM complexes increased, up to ~60 % of the total uranyl in the systems studied. Our results suggest a synergistic effect of NOM at pH 4.6, with a ternary complex forming that enhances uranyl sorption.