Mobilization of U from Noncrystalline U(IV) by Humic Substances under Anoxic Conditions

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Humic substances (HS), constituting a large component of natural organic matter (NOM), regulate many biogeochemical processes in the environment. Elevated levels of uranium (U) have been reported at numerous field sites abundant in NOM, such as contaminated wetlands, which are typically reducing. Yet, questions remain regarding the effect of HS on U mobilization from bioreduced U phases.

While HS have been shown to mobilize U from bioreduced field sediments, a knowledge gap exists regarding the reactivity of noncrystalline U(IV) (a dominant end-product of U bioreduction) in the presence of HS in model experiments. Additionally, the effect of calcium in diminishing dissolved organic carbon (DOC) concentrations available for U complexation (either through competitive binding or calciumenhanced aggregation) could play a decisive role in inhibiting U mobilization. Hence, in the current study, we aim to provide a basis for mechanistically understanding the effect of HS on the rate and extent of U mobilization from reduced U(IV) species under anoxic conditions. Specifically, experiments were carried out to elucidate the impact of HS on U mobilization from noncrystalline U(IV) using Suwannee River humic acid and fulvic acid across a range of environmentally-relevant concentrations at pH 7.0. The effect of calcium on HS-induced U mobilization was examined with both humic acid and fulvic acid. Additionally, U redox speciation in solution was measured in select treatments of humic acid and fulvic acid by ion exchange chromatography.

Fulvic acid and, to a greater extent, humic acid were shown to mobilize substantial levels of U from noncrystalline U(IV). While the majority of U mobilized was determined to be U(IV), U(VI) accounted for an appreciable level of the mobilized U. Interestingly, in experiments with calcium, significantly less U was mobilized (>75%). Through DOC measurements, we confirmed that competitive effects from calcium had a larger impact on inhibiting U mobilization than aggregation. These results provide mechanistic insights towards the stability of bioreduced U in the presence of HS. Furthermore, these findings highlight the increased risk of U mobilization in organic-rich environments while bringing to attention the influence of matrix effects (particularly competing metals) on U mobility from NOM.