

Update on the factors controlling the speciation of Hg and U in laboratory reactors, flow-through columns, and natural sediments

SBR - ANL SFA (Laboratory Research Manager: Robin Graham)

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The Argonne SFA aims to provide the molecular-level information needed for the development of predictive models that inform policy decisions. The focus here is on the mechanisms of U and Hg transformations in redox dynamic environments. Our previous studies demonstrated that Hg^{II} can be reduced to Hg^0 by several Fe^{II} species. Here we have tested the ability of Mn^{II} to reduce Hg^{II} . Results show that at pH 7.5, the majority of Hg^{II} is reduced to Hg^0 within three hours. Reduction of Hg^{II} is coupled to the oxidation of Mn^{II} to hexagonal birnessite (Mn^{IV}), which auto-catalyzes additional Mn^{II} oxidation. The reactivity of the birnessite phase is short-lived due to rapid evolution from the hexagonal to a triclinic polymorph, concomitant with a change to a slower rate of Hg^{II} reduction. These newly discovered mechanisms help improve Hg transport models and estimates of bioavailable Hg for methylation.

The redox transformations of U continue to be of interest due to the unknown structure and stability of the non-uraninite U^{IV} species observed in reduced sediments. We have shown that the mechanisms of U^{VI} bioreduction or the presence of trace phosphate exert significant control on the resulting U^{IV} species. We have also recently discovered that metal oxide surfaces can prevent uraninite formation and stabilize adsorbed U^{IV} . The molecular-level information accumulated on these distinct U^{IV} species is now allowing for a more precise identification of the non-uraninite U^{IV} species in contaminated sediments from the former Oak Ridge field site and of U^{IV} in naturally-reduced soils. Together with ongoing work on U^{IV} formation in the presence of clays, these results will enable an improved description of U^{IV} in transport models.

The Argonne SFA is also exploring the transformations of Fe, S, and contaminants under advective flow conditions. The initial studies here focus on comparing experimental profiles of Fe and S species in x-ray accessible columns to those predicted by reactive transport models. A column consisting of ferrihydrite-coated packing material and a sulfide-containing influent was used. The physical part of the transport model was defined by fitting the profiles of a Br tracer obtained by x-ray fluorescence measurements. The resulting dispersion coefficient was used in conjunction with a reactive network to predict Fe and S speciation along the flow path. The observed discrepancies between the measured and calculated profiles suggest the need for improvements in the reaction network based on the mechanistic information provided by the x-ray spectroscopy measurements.