

## Poster #22-20

### SLAC Groundwater Quality SFA: Mechanisms Controlling Colloid Formation and Impact on Water Quality in Alluvial Sediments

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Colloids help mediate the mobility of contaminants and nutrients in alluvial sediments that experience strong wet-dry redox cycling, which are common at SBR research sites. Here, we will present data suggesting that a large fraction of dissolved organic carbon in the saturated zone in alluvium along the Slate River, Gunnison Co, CO occurs is associated with iron sulfide colloids. Significantly, however, there are large gaps in our understanding of the nature of these colloids and parameters controlling their generation. In this study, we hypothesized that, during hydrological-redox transitions, oxidation of dissolved sulfides (onset of oxidizing conditions) or reductive dissolution of goethite and ferrihydrite (reducing conditions), releases organic carbon, metals, and anions, providing conditions ideal to generate colloids that can bind and mobilize U, Mo, Zn, and Pb. These are important alluvial contaminants at the Riverton, WY DOE legacy uranium ore processing site and at Slate River, within the LBNL Watershed Function SFA study domain. Knowledge of colloid formation and metal binding is needed to improve our understanding of how water quality will respond to hydrological changes such as drought and flooding.

Here, we examined the influence of sulfidation of Fe<sup>III</sup>-(oxyhydr)oxides nanoparticles associated with organic ligands on the generation, stability, and nature of colloids. We observed that reductive dissolution of ferrihydrite generated nanocluster colloids of mackinawite (FeS). Their subsequent aggregation, which promotes settling of mackinawite, was directly correlated to the concentration of sulfides relative to the iron oxides (S/Fe ratio). At low sulfide concentration (S/Fe ratio  $\leq 0.5$ ), the aggregation of mackinawite suspended nanoclusters took up to 14 days, indicating that during the first 14 days of sulfidation, colloids are able to bind and transport metals in groundwater. Inversely, at high sulfide concentration (S/Fe ratio  $> 0.5$ ) the sulfidation rate was rapid and the aggregation of mackinawite nanoclusters was accelerated, preventing generation of stable colloids. The presence of organic ligands can increase the time of residence of stable nanocluster colloids. The S/Fe ratio also controlled the concentration of DOC, which dramatically increased at high sulfide concentrations, thus promoting the mobility of organic-bound metals. Consequently, the effect on metal and actinide mobility and groundwater quality by sulfidation is dependent on the affinity of contaminants to bind to organic, Fe<sup>III</sup>-(oxyhydr)oxide, and mackinawite colloids, as well as the relative concentrations of these different phases. Elevated ionic strength accelerated nanocluster aggregation, inhibiting stable colloid generation. This investigation provides for the first time a general conceptual framework to predict the formation and reactivity of sulfidic nanoparticles in alluvial systems in response to wet-dry cycle perturbations.