

## Poster #21-54

### SLAC Groundwater Quality SFA: Contaminant Response to Hydrologic Transitions in Transiently-Reduced Zones

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Biogeochemical processes that govern metal and radionuclide mobility are highly sensitive to forcing by the water cycle. In the upper Colorado River Basin (CRB), water-saturated organic-enriched alluvial sediments locally exhibit reducing conditions and accumulate inorganic contaminants such as U, Zn, and Pb. Our research has shown that these so-called ‘naturally reduced zones’ (NRZs) commonly reside within the capillary fringe and are episodically or seasonally exposed to transient wetting and drying conditions. Because air enters pore spaces during capillary fringe ‘dry-down’, fluctuating hydrological conditions cause oxidation of NRZ sediments, creating conditions favorable to contaminant release. For example, oxidation of relatively insoluble U(IV) to soluble U(VI), as occurs in NRZs in the upper CRB, is generally thought to be an important mechanism of uranium mobilization. Knowledge of the interdependencies between hydrologic variability, sediment redox cycling, and contaminant import and export is requisite to model short- and long-term impacts on groundwater quality.

In this study, we tracked Fe, S, and U speciation to characterize the impact of hydrologic variability on redox processes and uranium speciation and mobility within fine-textured NRZ sediments in the capillary fringe at the Shiprock, NM DOE legacy site. As we have observed at other sites in the upper CRB, our results show that reducing conditions are needed to accumulate U in sediments. Surprisingly, however, our findings dispute the expectation that U predominantly accumulates as U(IV) in reduced sediments. Rather, we found that U accumulates as U(VI) at equal proportion to U(IV). The high abundance of crystalline U(VI) in reduced sediments suggests that redox cycling is needed to promote its accumulation, contradicting the common idea that U(VI) is lost during oxidation of sediments. We propose a new processes model for uranium mobilization in redox-cycled sediments where air-sensitive U(IV) is converted to crystalline U(VI) via a pathway that requires both hydrologic and redox variability under low permeability conditions.

In a related study, we have begun to investigate Zn speciation and stability in redox-active floodplains along the Slate River, Gunnison Co. CO, where it occurs as a contaminant at high sediment loadings (exceeding 1,000 mg/kg). Results to date suggest that Zn(II) is associated primarily with clay minerals within the transiently reduced zone and primarily with sulfides in the saturated zone. These findings suggest that Zn is stable during average seasonal wet-dry cycles. However, prolonged drying of the saturated zone, *e.g.*, during extended drought, could mobilize Zn due to sulfide oxidation.