

# Redox constraints on shallow alluvial sediments: Implications for U mobility

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Redox processes are important mediators of nutrient and contaminant storage in alluvial aquifers. Organic-enriched zones are common in sand-pebble-cobble aquifers in the Upper Colorado River Basin (UCRB) and develop Fe(III) and sulfate reducing conditions. We refer to these as “Naturally reduced zones” (NRZs). Large inventories of U accumulate in its reduced form, U(IV), in NRZs located within persistent U groundwater plumes, raising the likelihood that sediment-U interactions help to sustain these contaminant hot-spots. These reduced sediment bodies can subsequently act as secondary sources, releasing U back to the aquifer. The susceptibility of accumulated U(IV) to oxidation and remobilization creates the need to better understand and predict U speciation, the biogeochemical controls on redox conditions in NRZs, and their impact on U storage and remobilization.

In this study, we tracked Fe and S speciation in NRZs as a function of depth, organic carbon content, and grain size in order to better define the biogeochemical controls over the distribution and reactivity of redox process in the UCRB floodplain sediments. Redox reactivity was then compared with the distribution of U species in order to elucidate factors controlling their stability. Organic carbon content, moisture, and particle size of floodplain sediments were found to govern Fe and S mineral transformations and the abundance of reactive FeS and S(0) species in NRZs. Comparison of the distributions of these reactive species with that of U species suggests that: (i) iron sulfide occurrence maps on top of U(IV)-accumulating zones; (ii) reactive Fe(II) species relative abundance is a functional proxy to estimate susceptibility of NRZ U stocks to oxidative remobilization; (iii) Fe colloids are likely present and drive U(IV) remobilization under persistent reducing conditions. More specifically, investigations of these U(IV) pools in NRZs through UCRB corroborates the U behavior model in organic-enriched natural substrate simulating field conditions of these reducing zones that suggest that U(IV), resulting from abiotic and biologically mediated reduction of U(VI), adsorbs to the surfaces of particulate organic material and exhibits a molecular structure consistent with ‘non-crystalline’ U(IV) [1]. Our field investigation suggest that the preservation of these sensitive non-crystalline U(IV) pools depends on the properties of NRZs to protect these U(IV) pools from oxidative remobilization. We thus distinguish between (1) high-ability accumulating U, occurring when NRZ properties protect U from oxidative mobilization (“oxidation-resilient NRZ”) and (2) low-ability accumulating U corresponding to high susceptibility to oxidative remobilization (“oxidation-susceptible NRZ”).

[1] Bone et al., PNAS, 2017