A floodplain perspective on elemental cycling and uranium plume persistence

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Experiments at the Department of Energy's Rifle, CO (USA) field site have long focused on stimulated biogeochemical pathways arising from organic carbon injection. Although reductive pathways and their relation to uranium (U) immobilization have been a focus since 2002, ongoing studies are exploring oxidative pathways and their role in mediating fluxes of C, N, S, and aqueous metals. Insights gained from such 'stimulation' experiments are providing insight into analogous natural biogeochemical pathways that mediate elemental cycling in the absence of exogenous carbon. Such reactions are instead mediated by endogenous pools of natural organic matter (NOM) deposited during aggradation of aquifer sediments associated with fluvial processes within the Colorado River floodplain.

Discrete lenses of fine-grained, organic-rich sediments (up to 2% organic C and N) enriched in reduced species, such as Fe(II), iron sulfides and U(IV) have been identified along the active margin of the floodplain. Referred to as "naturally reduced zones" (NRZs), these localities constitute a distinct facies type (i.e., 'biogeofacies') within an otherwise gravel-dominated, largely NOM-deficient matrix. NRZs contain 100-fold higher U concentrations than surrounding aquifer sediments and represent 'hotspots' of seasonally intense C, N, S, and U cycling during excursions in groundwater elevation. Imbibition of air bubbles within the capillary fringe is inferred to contribute to seasonally oxic groundwater, with its impact on redox-mediated reactions exhibiting close correspondence to those induced through the intentional introduction of oxidants. Reactions induce sharp gradients in nitrate and sulfate resulting from elevated rates of nitrification and oxidation of reduced sulfur as dissolved oxygen becomes non-limiting. 7-fold increases in aqueous U are observed during this period likely contributing to U plume persistence.

Because NRZs contain large stores of NOM and have an outsized capacity to mediate redox transformations of relevance to U mobility, they are expected to exert influence over the redox status and biogeochemistry of contaminated floodplain deposits worldwide, with major implications for long-term contaminant bioavailability.