Combining hydrology and redox cycling: A new model to consider for U transport?

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Biogeochemical processes that govern metal and radionuclide mobility are highly sensitive to forcing by the water cycle. Episodic infiltration of oxidants to reduced zones can create biogeochemical hot moments that change microbial activity, initiate changes in sediment gas and water transport, and stimulate release of organic carbon, iron, and sulfur. In the upper Colorado River Basin, water-saturated organic-enriched sediments locally create reducing conditions that accumulate U. Subsequently, fluctuating hydrological conditions introduce oxidants which may reach internal portions of these sediments and reverse their role to secondary sources of U. Knowledge of the impact of hydrological variability on the alternating import and export of contaminants, including U, is the key requirement for predicting contaminant mobility and the short- and long-term impact on water quality.

In this study, we tracked U, Fe, and S speciation to characterize the variability in redox processes and related U mobility within the organic-enriched sediments of five U-contaminated floodplains along the upper Colorado River Basin. Our results suggest that U mobility is controlled not only by its molecular form and solubility, but also by variability in sediment permeability and organic carbon content. Together these factors regulate the exposure of U(IV) to oxidants and moderate its oxidative release. This results in a selective preservation mechanism based on susceptibilities of these species to oxidative remobilization, which control U species distribution. Further, our data suggests that hydrology driven by evapotranspiration and low permeability sediments promote conversion of U(IV) pools to crystalline U(VI) during intense redox oscillations, suggesting long-term U immobilization resistant to redox perturbation. This observation contradicts the common idea that U(IV) accumulated in reducing conditions is systematically released during re-oxidation. Our results emphasize the need for additional information regarding the impact of redox cycling driven by sediment physico-chemical combined with hydrology on the mobility of U and other redox-active contaminants, in order to predict their transport behavior from sediments to ground- and surface water.