Floodplain water quality is mediated by large seasonal changes in sediment water saturation, redox status, and the extent to which sediments interact and exchange solutes with groundwater. Strong spatial and temporal heterogeneities help mediate the availability and transport of redox active contaminants. For example, it has been postulated that inflow of oxygenated water into naturally reduced zones (NRZs) would stimulate oxidative release of U. However, recent laboratory experiments and field investigations suggest that oxygenation of groundwater can also lead to attenuation of U. In spite of their importance, the mechanisms and resilience of this effect have not yet been fully elucidated. Here we examine hydro-biogeochemical interactions to establish mechanistic controls over water quality in sediments experiencing influxes of oxygen.

In a dual domain column experiment, we used coarse grained aquifer material from the Riverton, WY, field site and inserted a varying number (0-3) of small spherical NRZs with elevated U concentrations and a natural background abundance of As. Oxygenated groundwater (without U for the first 8 weeks, then with U) was pumped through the columns and depth resolved pore water data was collected from inside NRZs and between them. Although we observed U loss from all NRZs, the same amount (or more) of U was retained in the aquifer material. This was attributed to sulfidic conditions having spread into the coarse-grained material around each NRZ. Consequently, Fe(II), As, and sulfides entered the groundwater around each NRZ, whereas U concentrations decreased with each NRZ encountered along the flow path. We conclude that high concentrations of sulfate in Riverton groundwater, together with the presence of soluble organic carbon in NRZs, sustained sulfate reduction inside NRZs; sulfide diffusion into the groundwater then drove oxygen consumption and reduction of Fe, As, and U. Thus, even small scale redox interfaces in S rich environments can strongly alter groundwater quality.

Another sulfide-bearing system experiencing strong redox fluctuations is the Pb- and Zn-contaminated alluvium along Slate River, CO. Seasonal (summer-fall 2018) measurements of dissolved solutes in pore water indicated strong variability that correlated with soil moisture content (and hence, oxygenation). Fe(II) concentrations declined more than 100-fold, while Zn increased more than 10-fold between moist (early-June) and dry (mid-August) conditions. X-ray microprobe analysis and X-ray absorption spectroscopy of Pb, Zn, and S showed that Pb and Zn are hosted by sulfide, Fe-oxide, and clay minerals, depending on depth and redox status, and that there is a strong vertical redox gradient. These results partially confirm our initial hypothesis that oxidative dissolution of sulfides drives the release of Zn, other metals, and organic carbon, thereby mediating water quality.