

## Decrease in Aqueous U(VI) Following an Influx of Oxidants into Organic-Rich Reduced Sediments

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**Project Abstract:** An existing paradigm describes that the influx of oxidants such as dissolved oxygen (DO) or nitrate will stimulate the oxidation of reduced chemical species such as iron, Fe(II), and uranium, U(IV). The change in redox state thus alters metal/radionuclide behavior and contributes to the generation of soluble and mobile U(VI) species influencing contaminant mobility. Field research results challenged the existing paradigm whereby low concentrations of an oxidant (DO) were directly amended into an alluvial aquifer and stimulated reducing conditions as well as a decrease in aqueous uranium concentrations (Rifle, CO; (Pan et al., 2018)). A series of laboratory experiments was initiated in batch reactors containing reduced, organic-rich, uranium bearing alluvial sediments (collected from Riverton, WY; SLAC SFA) test the impact of the influx of low oxidant concentrations (nitrate and DO) on uranium mobility. These reduced sediments were amended with anoxic bicarbonate buffered medium (Ar:CO<sub>2</sub>, 80:20; pH 6.7) with and without the addition of an oxidant (nitrate or DO). Aqueous U concentrations decreased (KPA and ICP-MS) following the addition of the oxidant, nitrate or DO. No significant decrease in aqueous U(VI) concentrations were observed in unamended controls. XANES analysis revealed an increase in solid-associated U(VI) in DO amended reactors. However, the inverse was true in nitrate amended reactors. XANES analysis of sediments collected from nitrate amended reactors revealed an increase in the amount of U(IV) relative to the unamended controls (85% U(IV) in treatment relative to 31% U(IV) in control). In addition to observing the reduction of uranium, a significantly higher concentration of aqueous Fe(II) was also observed in treatments relative to an unamended control indicating active Fe(III) reduction. Concurrent with an increase in aqueous Fe(II), a decrease in sulphide was observed. While this result could be indicative of oxidation, PHREEQC modelling of geochemical data supports the precipitation of Fe-sulphide as a potential mechanism for sulfide loss. All geochemical changes were observed concurrent with an increase in cell and virus abundance indicating cell growth and microbial activity. No significant changes were observed in controls. Together these results indicate that U retention under oxidizing conditions may not be solely limited to solid-phase sequestration of U(VI) but also an influx of an oxidant such as nitrate that can stimulate U(VI) reduction leading to sequestration as U(IV). This challenges our current understanding of U mobility in natural systems and indicates overlooked controls governing U redox cycling.

Pan, D., Williams, K. H., Robbins, M., and Weber, K. A., 2018, Uranium Retention in a Bioreduced Region of an Alluvial Aquifer Induced by the Influx of Dissolved Oxygen *Environ Sci Technol*, v. 52, no. 15, p. 8133–8145.