ABSTRACT: As the most ubiquitous contaminant anion in groundwater sediments at US DOE sites, high levels of nitrate (NO₃⁻) also co-occur with one or more priority contaminant metals or radionuclides. This project seeks to improve our understanding of subsurface biogeochemical nitrogen cycling and its multifaceted interactions with redox-active elements, in particular iron, in order to better predict the fate and transport of the widespread radionuclide uranium (U) in complex subsurface environments. In particular, bioremediation efforts focused on immobilizing U through stimulation of microbial reduction of U(VI) to U(IV) are inhibited by the presence of NO₃⁻. Furthermore, the potential for introduction of nitrate-contaminated groundwater poses a direct and serious threat to the stability of uranium immobilization in subsurface sediments both directly, through the oxidation of U(IV) by NO₃⁻ and/or the reductive intermediate NO₂⁻, or indirectly by coupling of N and Fe cycling. As such, the interpretation of the results of field-scale bioremediation studies are often complicated by the fact that several competing processes occur simultaneously. Through the use of new and integrated multi-isotope tools, which represent naturally occurring spatial and temporal integrators of cycling processes, this project aims to improve the detection of biogeochemical changes in the subsurface, particularly those involving the direct and/or indirect coupling of nitrogen cycling to U(IV) oxidation and mobilization. Specifically, the use of coupled isotope systems (e.g. ¹⁵N/¹⁴N and ¹⁸O/¹⁶O and the ratio of their respective isotopic fractionation or ¹⁸ε¹⁵N: ¹⁵ε¹⁸O) provides an even more powerful constraint on quantifying the relative roles of simultaneously occurring cycling processes in the context of subsurface redox transformations, including those responsible for U mobilization.

Experiments were conducted to characterize the N and O kinetic isotope effects of abiotic reduction of both NO₃⁻ and NO₂⁻ by Fe(II) as a starting point for characterizing linkages among subsurface N, Fe and U cycling at the field-scale. Results indicate substantial reduction of both NO₃⁻ and NO₂⁻ by Fe(II) in both the presence or absence of iron oxyhydroxides minerals. A range of N and O kinetic isotope effects (for both NO₃⁻ and NO₂⁻) were observed across experimental conditions (¹⁵ε NO₃⁻ = 6.8 to 32.7‰, ¹⁸ε NO₃⁻ = 3.4 to 19.7‰; ¹⁵ε NO₂⁻ ~11.5‰, ¹⁸ε NO₂⁻ ~4-6‰). Importantly, in all cases, abiotic reduction of either NO₃⁻ or NO₂⁻ by Fe(II) exhibited smaller O isotope effects than N isotope effects (¹⁸ε: ¹⁵ε = 0.4 to 0.7). In contrast to canonical denitrification (¹⁸ε: ¹⁵ε = 1), values of ¹⁸ε: ¹⁵ε in NO₃⁻-contaminated groundwaters commonly fall between 0.5 and 0.8. As such, our results point to a potentially widespread importance of Fe (II) based N reduction in these environments.

During the next phase of characterization, a series of 17 flow-through natural sediment columns was run for ~60 days under reducing conditions. In a subset of columns, Fe reduction was allowed to occur for 30 days, followed by the addition of NO₃⁻. Multi-isotope data showed prominent shifts in ¹⁸ε: ¹⁵ε over the course of NO₃⁻ addition and are interpreted as reflecting a shift from an initial Fe(II)-based reduction of NO₃⁻ to NH₄⁺ to the onset of biological denitrification (NO₃⁻ reduction to N₂). Based on these results, we posit that tracking changes in NO₃⁻ and NO₂⁻ concentration and δ¹⁵N and δ¹⁸O along with aqueous and solid phase U and Fe chemistry in future experiments will allow partitioning of the specific N reducing processes directly and indirectly related to U(IV) reoxidation and mobilization under advective flow.