ABSTRACT: Diverse groups of microorganisms and abiotic reactions affect the oxidation state of redox-active metals, and oxic-anoxic transition zones are hotspots for metal cycling. Redox transition zone processes are relevant controls for the fate of radionuclides such as uranium, which is mobile as U(VI) but only sparingly soluble in its U(IV) form. Metal-reducing bacteria adapted to life in oxic-anoxic transition zones play important roles for controlling U mobility. To explore the effects of changing redox conditions on the microbiology contributing to ferric iron and U(VI) reduction, an x-ray accessible plexiglass column with sampling and outflow ports along the length of the column has been constructed. Initial tests of the column packed with acid washed sand and FeOOH-coated sand showed that changes in the distribution and speciation of Fe resulting from the flow of dissolved sulfide can be monitored with synchrotron x-ray spectroscopy using the intact column. Another column design allows the infusion of different (e.g., oxic and anoxic) feed solutions from both ends leading to the formation of a controllable redox gradient and is being used to investigate the responses of microbes to fluctuating oxic-anoxic transition zones.

A number of microbes have been implicated in metal reduction and tools to directly measure their metal-reducing activity are desirable. We applied high precision mass spectrometry and demonstrated that a significant U isotopic fractionation occurs during microbial U(VI) reduction, with U(VI) becoming isotopically lighter with progressive amounts of reduction. Enrichment factors (ε) measured with different metal-reducing isolates (i.e. Geobacter, Anaeromyxobacter, Shewanella and Desulfitobacterium) tend to range between 0.7‰ and 1.0‰, and follow the expected inverse relationship between reaction rate and the magnitude of fractionation. Only Shewanella sp. strain NR exhibited unusual near-zero fractionation at low U concentrations, suggesting that multiple U reduction pathways with different mechanisms (and thus different isotopic fractionation) contribute to U(VI) reduction. Further, metaproteomics analysis identified specific c-type cytochromes expressed in cultures of Anaeromyxobacter dehalogenans strain 2CP-C grown with manganese oxide as electron acceptor suggesting that the presence and abundance of the specific transcripts and/or proteins provides information about the physiological status of the organism. The analysis of samples obtained from defined laboratory studies and groundwater samples collected at field sites demonstrates the value of the new tools to assess, monitor, and predict reductive processes affecting the redox speciation (i.e., mobility) of relevant metals and radionuclides.