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ABSTRACT TITLE: Field observation of uranium sequestration in iron-rich sediments under sequential reduction-oxidation conditions at the DOE Oak Ridge IFRC

ABSTRACT: At the U.S. DOE Oak Ridge Integrated Field Research Challenge (ORIFRC) site, the iron content of shallow subsurface materials (i.e. weathered saprolite) is relatively high (up to 5-6% by weight), and iron species play a critical role in the long-term sequestration of uranium. To assess the role of iron on U sequestration under field conditions, we monitored U(VI) levels in groundwater after pilot-scale bioreduction and reoxidation experiments conducted at the ORIFRC area 3 site, adjacent to the former S-3 disposal ponds (source zone). In a previous experiment to assess bioreduction, aqueous U(VI) concentrations at the site decreased to levels less than the EPA MCL following intermittent injection of ethanol as the electron donor. When the oxidants oxygen and nitrate were then allowed to enter the bioreduced zone, bioreduced U(IV) was oxidized resulting in a temporary rebound in aqueous phase uranium concentrations.

To understand the long-term effect of oxidant exposure, a field test was conducted with bioreduced sediments exposed to nitrate for more than 1,380 days within Area 3. Nitratecontaminated groundwater was allowed to enter a previously bioreduced zone via the natural groundwater gradient. The geochemical response to this contaminated groundwater was dependent upon the monitoring location: in general, nitrate concentrations entering the previously bioreduced area increased gradually from near zero to ~50-300 mM within 200 days then stabilized. The pH declined from levels of 6.2-6.7 following bioreduction to <5.0. Uranium concentrations rebounded in all monitoring wells but at different rates. At most locations, U concentrations rebounded, declined, then rebounded a second time. Methane gas disappeared while N2O levels increased dramatically (from levels below detection to 20,000 - 44,000 ppmv) at monitoring wells subject to three years of niitrate exposure.

The U(IV) in sediments was mainly reoxidized to U(VI) species. XANES analyses indicated that the dominant form of uranium after re-oxidation was a mixture of uranyl carbonate and U(IV) bound to Fe bearing phases. The U content in the sediments remained as high as that measured after bioreduction, indicating that much of the U remained sequestered *in situ*. SEM observations of surged fine sediments revealed clusters of colloidal-sized precipitates (200-500 nm) containing uranium. These particles appeared to have formed in situ, and were present in a control area that received no ethanol addition and in previously bioreduced sediment. XRF analyses of sediment sampled after after three years of oxidation revealed that the U content on previously bioreduced sediment was as high or higher than values measured just after bioreduction, ~2000 mg/kg, indicating long-term U sequestratration in pre-bioreduced sediments. The microbial community before and after the re-oxidation was also analyzed to elucidate the impacts of geochemical changes on subsurface microbiology.