Long-term uranium sequestration as nitrate invades a previously reduced zone - DOE Oak Ridge IFRC site

Weimin Wu (billwu@stanford.edu) - Stanford University, Craig S. Criddle (PI).

W.-M. Wu, C. Criddle- Stanford University, D. Watson, T. Mehlhorn, K.Lowe, J. Phillips, J. Earles, G.-P. Tang- Oak Ridge National Laboratory, B. Li, Y.-Q. Chao, T. Zhang- The University of Hong Kong, D. H. Phillips- Queen's University of Belfast, S.D. Kelly-EXAFS Analysis, P.-S.Li, H.-C.Tao-Peking University Shenzhen Graduate School, Z.-B. Chen- Dalian Nationalities University. A long term pilot-scale study of in-situ U(VI) sequestration was conducted at a site at the U.S. DOE Y-12 National Security Complex, Oak Ridge, TN. The contaminated sediments contained up to 5-6% of iron and 700-1000 mg U/kg dry weight with groundwater U of ~20-40 mg/L. U concentrations lower than the US EPA MCL (0.03 mg/L) were achieved through bioreduction treatments using intermittent injection of ethanol. Since the end of the bioreduction study, we have examined the long-term effect of exposure of the bioreduced sediments to nitrate from the natural influx of contaminated groundwater for > 1,500 days. Vertical and horizontal spatial differences in the increase (recovery) of U concentration and biogeochemical response to the influx of groundwater were observed. In general, the nitrate concentrations in the previously bioreduced area increased gradually from near zero to ~50-300 mM and then stabilized. The pH declined from the bioreduced levels of 6.2-6.7 to below 5.0. U concentrations in the bioreduced zone typically rebounded, declined and then rebounded again. The U(IV) in sediments was reoxidized to U(VI) species according to XANES analysis but the Uranium content in the sediment remained as high as previously identified. SEM-EDX analysis of reoxidized sediment samples revealed clusters of U containing carbonate precipitates (~1-2% U, w/w) that also contain high amounts of Fe, Al and Si, indicating that at least some U was still sequestrated in-situ after the reintroduction of contaminated oxic groundwater. Significant levels (>100000 ppmv) of N2O was found in groundwater after reoxidation. The impact of geochemical change on subsurface microbiology was investigated by 454 pyrosequencing analysis of the sediment samples. Significant community shifts occurred after the re-oxidation. The bioreduced communities dominated by sulfate-reducing (Desulfovibrio) and iron reducing (Geobacter and Geothrix) bacteria shifted to denitrifying Rhodanobacter, iron(II) oxidizing Phizomicrobium as well as denitrifying Castellaniella under more oxic conditions. However, the U(VI)-reducing, spore-forming sulfate reducing bacteria, Desulfosporosinus remained abundant under the oxic conditions. These observations indicate significant U sequestration continued after the oxidative agent nitrate invaded the bioreduced area.