

A meso-scale laboratory study of stable isotope variations during uranium bioremediation

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We present results from a large-scale column experiment designed to bridge the gap between the field scale and small columns and advance our understanding of the isotopic signatures of biostimulation geochemistry. Stable isotope variations of major elements such as C, Ca and S can identify processes unobservable in concentration data alone but an understanding of these isotope systems must first be developed under controlled biostimulation conditions.

A 1m long, 10cm diameter column was packed with sediment from the saturated zone of the Rifle Integrated Field-Scale Subsurface Research Challenge (IFRC) site in western Colorado. The pore velocity of the column experiment was matched to that of the field, thus providing a direct representation of the first meter down-gradient of the *in situ* uranium bioremediation injection gallery while ensuring steady flow and boundary conditions. Side-ports along the length of the column provided <20cm sampling resolution, while inert tracers and electron donor were added to the injection solution.

This study has generated an extensive isotopic and biogeochemical reactive transport dataset and provides an unprecedented opportunity to constrain carbon, calcium and sulfur isotopic dynamics. Results include:

- 1) $\delta^2\text{H}$ and $\delta^{18}\text{O}$ breakthrough curves yielding a starting porosity of 0.38 decreasing to 0.30 over 42 days.
- 2) $\delta^{13}\text{C}$ -labeled acetate allows tracking of carbon originating from electron donor consumption throughout the system.
- 3) $\delta^{44}\text{Ca}$ variations in the fluid phase identify two primary controls on Ca: precipitation of carbonates and ion exchange between the fluid and sediment.
- 4) A $\delta^{34}\text{S}$ fractionation factor of 12‰ between SO_4^{2-} and HS^- in comparison with a Rayleigh model α of 10‰ indicates variation in α values across the flow path.

These observations are a direct result of the improved spatial and temporal sampling resolution afforded by the experimental design and allow new insight into the highly reactive zone adjacent to contaminant remediation injection wells.

Redox front variability and phosphorus flux across the sediment-water interface

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Phosphorus mobility across the sediment-water interface (SWI) in Missisquoi Bay, a shallow (<15m) bay in Lake Champlain, is largely controlled by redox changes exhibiting diel and seasonal variability that can significantly impact nutrient fluxes and associated cyanobacterial activity. In these iron rich (4-5% w/w total Fe) sediments, reactive P (RP) is strongly correlated to reactive Fe, indicating the mobility of a large portion (30-40%) of the P pool in the sediment is associated with iron oxyhydroxide minerals. We investigated changes in sediments, sediment porewaters, and the overlying water column chemistry and microbiology over three consecutive seasons with detailed monitoring of diel changes at the SWI at each sampling time. Sediment cores were profiled using voltammetric electrodes to characterize porewater redox chemistry (O_2 , Mn^{2+} , Fe^{2+} , Fe^{3+} , HS^- , $\text{FeS}_{(\text{aq})}$). Core profiles show redox conditions become more reducing as the season progresses, with the most strongly reducing conditions present during peak bloom conditions. Redox conditions measured continually over 24-hour periods using *in situ* voltammetric electrodes positioned at the SWI showed significant changes in redox conditions over diel cycles. Cluster analysis of the data using self-organized mapping techniques indicate redox chemistry across the SWI is a significant controlling component of the system that influences cyanobacterial blooms.

As P fluxes are sensitive to a thin layer of iron oxyhydroxides at the sediment surface, changes in redox chemistry at the SWI significantly impact nutrient flux between the sediment porewaters and the overlying water column. Mesocosm experiments utilizing Missisquoi Bay sediments are underway to characterize phosphorus fluxes between the sediments and water column under different redox conditions at the SWI. Preliminary results indicate that both the direction and intensity of P flux across the SWI are dependent on the redox front position and the frequency of how often the redox front sweeps across the SWI.