ABSTRACT TITLE: Development of U isotope fractionation as an indicator of U(VI) reduction in U plumes

ABSTRACT: We are evaluating $^{238}\text{U}/^{235}\text{U}$ (as $\delta^{238}\text{U}$) as a tool for monitoring U(VI) reduction in the controlled field setting at the Rifle, CO IFRC site. Understanding the biogeochemical behavior of uranium in the subsurface will help to improve remedial strategies and long-term stewardship activities at DOE sites. We present $^{238}\text{U}/^{235}\text{U}$ (as $\delta^{238}\text{U}$) results for three Rifle IFRC field experiments: (1) the 2010–11 experiment, which combined bicarbonate-induced desorption of U(VI) and down-gradient acetate-induced bioreduction (21 and 25 days, respectively), (2) the subsequent 2011–12 experiment, which evaluated the impacts of prolonged bicarbonate and acetate amendments (94 and 72 days, respectively) and the impact of a second acetate injection and (3) the 2012–2013 reoxidation experiment.

Large variations in $\delta^{238}\text{U}$ accompany acetate-induced biostimulation under both iron reducing (2010–11) and sulfate reducing conditions (2011–12). In both cases, $^{238}\text{U}$ is preferentially reduced to U(IV), leaving the remaining groundwater U(VI) relatively enriched in $^{235}\text{U}$ ($\Delta^{238}\text{U} = -1.3$ and $-1.9\%$, respectively). Thus $\delta^{238}\text{U}$ in waters decreases as the U concentration drops from $\sim$150–200 ppb U prior to the acetate injection to $\sim$10 ppb after. For the 2010–11 experiment, groundwater U(VI) concentration and $\delta^{238}\text{U}$ quickly return in unison to background values within 113 days after the end of the acetate injection. During the post-injection phase, as concentrations rebounded, absence of $^{238}\text{U}/^{235}\text{U}$ greater than pre-injection values implies the primary source of U is advection of U(VI), rather than reoxidation of U(IV). This is particularly important as the long term success of this remediation technique depends on the stability of sequestered U(IV). Early results from the 2012–2013 reoxidation experiment suggest that as the dissolved oxygen injection proceeded, oxidation of U(IV) precipitates leads to both an increase in U concentration and $^{238}\text{U}/^{235}\text{U}$ of groundwater.

For 2010–11 samples impacted by both bicarbonate and acetate amendments, we observe an initial increase in U(VI) concentration (more than doubling) due to the bicarbonate desorption of U(VI) from mineral surfaces followed by a large drop in U(VI) concentration as acetate-induced reduction proceeds. As with the bicarbonate-only desorption experiment [1], U(VI) desorption resulted in no change in $^{238}\text{U}/^{235}\text{U}$; this ratio, however, changes with the onset of reduction with acetate amendment. $\delta^{238}\text{U}$ decreases quickly, then rebounds during the time of lowest dissolved U(VI) concentration, and finally increases slowly to background levels within 266 days from the end of the acetate injection. The much slower recovery is suggested to result from the slow exchange of newly advected U with the relatively light sorbed U (resulting from equilibration of sorption sites with light dissolved U(VI) during the biostimulation). Thus, bicarbonate-induced U desorption in combination with biostimulation increases the removal of U(VI) during biostimulation.

Our research demonstrates the potential for $^{238}\text{U}/^{235}\text{U}$ to detect U(VI) reduction in the subsurface and to distinguish between removal by reduction and relatively temporary processes such as sorption. Preliminary results from the latest experiment at Rifle suggest the $^{238}\text{U}/^{235}\text{U}$ technique can also be used to detect reoxidation of previously sequestered U.