238U/235U as an indicator of re-oxidation of U(IV) in the subsurface of remediated sites

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At the controlled field setting at the Rifle, CO IFRC site, acetate-induced biostimulated reduction of U has been demonstrated to be accompanied by large variations in 238U/235U (discussed as Î´238U). Under both iron reducing and sulfate reducing conditions, 238U is preferentially reduced to U(IV), leaving the remaining groundwater U(VI) relatively enriched in 235U with shifts in the Î´238U of ˆ'1.3 and -1.9‰, respectively, for a >90% apparent U(VI) loss.

The long-term success of biostimulation as a remediation technique depends on the stability of sequestered U(IV). Uranium is readily oxidized by dissolved oxygen (DO) and other oxidants, such as nitrate, MnO2, and ferrihydrite, posing a problem for long-term bioremediation efficacy. Because reduction of U(VI) deposits isotopically heavy U(IV), remobilization of this U(IV) has the potential to be detected when this isotopically heavy U is added back into the dissolved U(VI) pool. To assess changes in U concentration and 238U/235U accompanying re-oxidation, we present the results for two Rifle IFRC field re-oxidation experiments with dissolved oxygen (DO) and nitrate as the oxidants.

In both experiments, an oxidant (i.e., DO or nitrate) was injected into a previously biostimulated plot. Both DO and nitrate injections led to U concentration increases (up to 270 and 558 ppb, respectively), well above that of inflowing upgradient groundwater (~175 ppb). For the DO injection, U concentration increases were accompanied by a significant increase in Î´238U from -0.60‰ to 0.00‰, possibly indicative of re-oxidation of isotopically heavy U(IV). However, despite the clear increase in the Î´238U, re-oxidized U(IV) cannot be identified definitively as the source because the DO injection experiment began during the time the experimental plot was recovering from acetate-induced reduction (i.e., the Î´238U was still isotopically lighter than upgradient groundwater). However, the nitrate injection reveals for the first time a significant increase in Î´238U from ~0.00‰ to 0.50‰, well above that of upgradient water (0.02‰). This clearly indicates re-oxidation of isotopically heavy U(IV) as hypothesized.

Our research demonstrates the potential for 238U/235U measurements to detect re-oxidation of previously sequestered isotopically heavy U(IV) in the subsurface and to distinguish between U(VI) additions from re-oxidation and other processes such as desorption. These results contribute to the development of 238U/235U as a powerful tool in the assessment of the effectiveness of U bioremediation efforts.