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

University-Led Research

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We are evaluating U isotope ratios ($\delta^{238}U$) as a tool for monitoring U(VI) reduction in the controlled field setting at the Rifle, CO IFRC site. The increased understanding of the biogeochemical behavior of U can guide remedial strategies and long-term stewardship activities at DOE sites. Several key questions are under investigation: (1) Are there confounding processes that complicate efforts to use $^{238}U/^{235}U$ as an indicator of U(VI) reduction (e.g., adsorption, mixing of distinct U from different flow paths)? (2) Is the U isotopic fractionation factor ($\varepsilon = (\alpha\text{-}1) \times 10^3$; $\alpha = {}^{238}U/^{235}U_{product}/^{238}U/^{235}U_{reactant}$) for U(VI) reduction constant? (3) Does the fractionation factor for U(VI) reduction differ between natural and stimulated conditions? (4) How do effective (field experiments) and intrinsic (laboratory experiments) fractionation factors compare? (5) Can reoxidation be detected using $^{238}U/^{235}U$? (6) Can biotic and abiotic reduction be distinguished by $^{238}U/^{235}U$?

$\delta^{238}U$ was measured in groundwater samples from the 2010–11 experiment to evaluate the degree of isotopic fractionation due to (1) bicarbonate induced U(VI) desorption and (2) acetate amended U(VI) reduction (occurring with or without bicarbonate amendment). Samples from a well impacted only by bicarbonate amendment reveal no significant U isotopic fractionation resulting from adsorption/desorption of U(VI) from aquifer solids. Samples from a well impacted by only acetate amendment show a similar shift in $\delta^{238}U$ to that observed for the 2007 biostimulation experiment [1] ($\Delta^{238}U$ =1.35‰ and 1.05‰, respectively), where ^{238}U is preferentially removed as reduced U(IV). In addition, the 2010–11 results give us, for the first time, $\delta^{238}U$ measurements during rebound of U(VI) concentrations after acetate amendment is terminated. In a well impacted only by acetate amendment, groundwater U(VI) concentration and $\delta^{238}U$ return to preinjection values within 128 days. Lack of an increase of $\delta^{238}U$ above preinjection 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). Notably, the recovery of U(VI) concentration and $\delta^{238}U$ is much slower for a well impacted by both bicarbonate and acetate amendments; by 201 days after acetate injection stopped, U(VI) concentrations returned to preinjection values, yet $\delta^{238}U$ remained significantly lower (-0.43‰) than initial conditions, possibly reflecting resorption of upgradient U.

Rifle floodplain samples exhibit limited but significant variation in U concentration and $\delta^{238}U$. The three surface waters collected north of the site are characterized by a mean U concentration and $\delta^{238}U$ of 36.9 ppb and -0.12‰, respectively. Similarly, the background well LR01 (not impacted by mill operations) is characterized by a U concentration and $\delta^{238}U$ of 44.5 ppb and -0.19‰, respectively. The remaining site floodplain samples exhibited significantly higher U concentrations ranging from 111 to 327 ppb and $\delta^{238}U$ from -0.05 to 0.24‰. The total variation, 0.43‰, is greater than the long-term uncertainty, 0.09‰ (2× root mean square difference between measurements of 16 full sample duplicates). Among floodplain samples, as the U concentration increases, a corresponding increase is observed in the $\delta^{238}U$ value. This relationship may be due to mixing between background U coming into the site with contaminant U remaining from historical U mill operations.

[1] Bopp, C.J. et al. (2010) Environ. Sci. Technol. 44, 5927–5933.