

## **$^{238}\text{U}/^{235}\text{U}$ changes in groundwater associated with re-oxidation of reductively immobilized uranium**

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Uranium is soluble, relatively mobile and toxic in its oxidized state, U(VI). In contrast, U is relatively insoluble and generally immobile in its reduced state, U(IV). This has led to the pursuit of U(VI) reduction as a remedial strategy for contaminated groundwater. Both laboratory and field studies have revealed that the rate of  $^{238}\text{U}$  removal is slightly higher than that of  $^{235}\text{U}$  for microbial U(VI) reduction (discussed as  $\delta^{238}\text{U}$ ). At the former U mill site in Rifle, CO (USA), acetate-induced biostimulation (under both iron and sulfate reducing conditions) results in shifts in the  $\delta^{238}\text{U}$  of U(VI) of  $-1.3$  and  $-1.9\text{‰}$ , respectively, for a  $>90\%$  apparent U(VI) loss. These changes in  $^{238}\text{U}/^{235}\text{U}$  accompany large changes in U concentration (dropping from 150–200 ppb U to  $\sim 10$  ppb U) and demonstrate the use of  $^{238}\text{U}/^{235}\text{U}$  to detect and quantify the extent of U(VI) reduction in groundwater.

Uranium is readily oxidized by dissolved oxygen (DO) and other oxidants, such as nitrate,  $\text{MnO}_2$ , and ferrihydrite, posing a problem for long-term bioremediation efficacy. Because reduction of U(VI) deposits isotopically heavy U(IV) toward the upgradient side of the reduction zone, remobilization of this U has the potential to reveal itself in the form of isotopically heavy dissolved U(VI) should oxidation accompany the cessation of active remediation and a rebound in aquifer redox status.

To examine changes in U concentration and  $^{238}\text{U}/^{235}\text{U}$  accompanying re-oxidation, we present results of two field experiments (2012 and 2013) performed at the Rifle site. In both experiments, an oxidant (DO and nitrate, respectively) was injected into a previously biostimulated plot (2011 and 2012). Both DO and nitrate injections led to U concentration increases (up to 270 and 550 ppb, respectively), well above that of upgradient groundwater ( $\sim 175$  ppb). For the DO injection, U concentration increases were accompanied by increasing  $\delta^{238}\text{U}$  from  $-0.60\text{‰}$  to  $0.00\text{‰}$ , possibly indicative of re-oxidation of isotopically heavy U(IV).  $\delta^{238}\text{U}$  results from the nitrate injection will provide additional clarification.

This study provides the first examination of U isotope systematics during re-oxidation in the field and thus contributes to the development of  $^{238}\text{U}/^{235}\text{U}$  as a valuable tool for assessing U bioremediation efforts.