

## Reactivity of Tc at the Groundwater-Surface Water Interface

JOHN M. ZACHARA<sup>1\*</sup>, JIM FREDRICKSON<sup>1</sup>  
AND JIM MCKINLEY<sup>1</sup>

<sup>1</sup>Pacific Northwest National Laboratory, Richland, WA 99352  
(\*correspondence: john.zachara@pnl.gov)

Technetium-99 ( $t^{1/2} = 211,000\text{y}$ ) is mobile in the environment as the pertechnetate oxyanion [ $^{99}\text{Tc(VII)O}_4^-$ ]<sub>(aq)</sub>. Tc(VII) may react to less soluble Tc(IV) at intermediate redox potentials ( $E^\circ = -0.36\text{ V}$ ) through heterogeneous reduction.  $^{99}\text{Tc}$  is forecast to migrate through groundwater to the Columbia River at the U.S. DOE Hanford site in Washington State. Discharge to surface water will occur through a groundwater-surface water interaction zone with complex hydrogeology and biogeochemistry. The reactivity of pertechnetate in reduced sediments from this zone was investigated to determine effects of ferrous-Fe and sulfide-S on Tc(VII) reduction rate, and the resulting speciation and mineral association.

$^{99}\text{Tc(VII)}$  was reduced to near or below detection over periods of days to months. Tc(VII) reduction rate was first order in  $[\text{Tc(VII)}]_{\text{aq}}$  and sediment mass, but correlations with specific reductant concentrations  $[(\text{Fe(II)}, \text{AVS})]$  were not found. Tc(IV) was isolated to aggregates of primary mineral material embedded within a fine-grained phyllosilicate matrix. EXAFS revealed that product Tc(IV) existed as combinations of a Tc(IV)O<sub>2</sub>-like phase, Tc(IV)-Fe surface clusters, and/or TcS<sub>x</sub>. AVS was implicated as a more selective reductant. Aggregates were reaction centers in the coarse-textured sediments regardless of the dominant anoxic biogeochemical process.