A Physiochemical Analysis of the Transport and Retention of Technetium in Unsaturated Hanford Formation Sediments

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The transport of Tc, like many other radionuclides, is of interest due to the potential for human exposure and impact on ecosystems. Specifically, Tc is a contaminant of concern at several DOE facilities including the Hanford, Oak Ridge, Paducah, Portsmouth, and Savannah River Sites.

Current conceptual models do not fully explain the distribution and persistence of technetium in vadose zone environments such as the Hanford site, Eastern Washington. In an oxic environment with low organic content the residence time of technetium in the soil would be expected to be low, due to its low sorption and high mobility. While $Tc^{VII}O_4$ can be reduced, it is also readily oxidized, so temporary reducing environments are not expected to alter the general rapid Tc migration in the subsurface. Inexplicably, nearly 50 years following the release of contamination into the site, a significant fraction of Tc has persisted in the subsurface in the 200 Area.

In these experiments we examined the unsaturated transport of pertechnetate at very low water content using an Unsaturated Flow Apparatus (UFA) to evaluate breakthrough curve behavior and the potential impact of immobile domains, anion exclusion and sorption on the transport and retention of technetium. The analysis confirmed that Tc was transported at pore water velocity and that transport was not altered by the presence of immobile domains, anion exclusion, or sorption. The experimental dispersivity increased with decreasing saturation.

Using borehole sediments from the Hanford site 200 Area where Tc was co-disposed with a variety of chemicals and has been in contact with the sediment for decades, a series of sequential extractions was conducted to evaluate the mineral associations of technetium in natural Hanford sediments. The sequential extractions targeted the Tc associated with the ion exchange layer, carbonate minerals, aluminosilicate minerals and iron oxides. The analyses indicated that while most Tc was associated with an aqueous extractable phase, some Tc was associated with oxalic acid and nitric acid extractable phases. The preliminary results indicate a portion of the Tc may be less mobile than originally indicated. EXAFS and XANES will be used to identify Tc surface phases, as the surface Tc may be incorporated in minerals or coated by non-Tc precipitates. Results from extractions and additional geochemical analysis will be presented.

Saline groundwater discharges in the Athabasca oil sands region: a chemical mass balance

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Quantifying water quality impacts of oil sands developments in western Canada will require decoupling natural contributions of organic and inorganic contaminants from potential releases from tailings ponds, oil sands mining, and in-situ bitumen production. Here, we quantify natural saline groundwater contributions to the Athabasca River by applying a chemical mass balance (Cl^-) to monthly chemical and discharge data collected between 1987 and 2009, using data available from the Long Term River Network.

The results of the chemical mass balance indicate that saline springs are an important control on the chemistry of the Athabasca River, despite comprising <3% of the river's discharge. The impact of these discharges on the chemistry of the Athabasca River is greatest during periods of low river flow. The shift in chloride concentrations measured between Fort McMurray and the Peace Athabasca Delta can only be explained if saline groundwater along this stretch are in the range of 500 to 3400 L/s. This finding is supported by the subcrop exposure and known seepage of Devonian- and Cretaceous-aged aquifers bearing saline fluids along this reach of the Athabasca River. While this study does not exclude the possibility that tailings discharge to the Athabasca River could be occurring, the observed increase in chloride measured between Fort McMurray and the Peace-Athabasca Delta cannot be accounted for using tailings pond seepages alone. The range of chloride concentrations reported for a wide range of tailings ponds are very low in comparison with the groundwater seeps entering the river and the total increase in chloride along this stretch cannot be reconciled using just mixing with tailings pond water.

Given the important role discharges of saline groundwater from Cretaceous and Devonian formations appears to play in the geochemical evolution of the Athabasca River, a more comprehensive evaluation of regional groundwater flowpaths and groundwater surface water interactions is warranted. These results suggest that any future water quality monitoring efforts for the Athabasca River should try to better quantify the contribution of groundwater inflow to changes in river water quality.