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Redox zonation and biogeochemical cycling in contaminated subsurface systems: Application of a new 3D partial-equilibrium model BGTK

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Biogeochemical data collected from a contaminated aquifer at the former Wurtsmith Air Force Base in Oscoda, MI, USA suggests that under steady-state, "mature" plume conditions, traditional redox zonation may not be a realistic model of the distribution of terminal electron accepting processes (TEAPs) and thus may not be the best model to evaluate potential degradation rates of organic compounds. Based on these data, a conceptual model of TEAP evolution in reduced subsurface systems was developed. This model proposes that during initial plume development electron acceptors O₂, Fe³⁺, NO₃, and SO₄ are consumed sequentially based on thermodynamics until a balance between source inputs and organic degradation rates and thus a stable plume length can be achieved. Once this "mature" state has been achieved, distinct redox zones can no longer be sustained and methanogenesis will dominate except in portions of the aquifer impacted by recharge water and diffusion of electron acceptors at small-scale mixing interfaces. Recent data collected from a contaminated wetland/aquifer system at a closed municipal landfill in Norman, OK, USA supports the concept that mixing interfaces between waters of differing redox potential are zones of increased rates of TEAPs.

A new 3-D partial equilibrium model **BGTK** was used to quantitatively evaluate our conceptual model[1]. Hydrologic, microbiologic, and geochemical data were combined using high-resolution mechanistic models that incorporate measured kinetic and equilibrium controls on reactions. Our model is based on the well tested packages RT3D[2] and PHREEQC[3]. This new model allows for 1) biodegradation of organic matter based on the influence of transport processes on microbial metabolism; 2) representation of steep hydro-bio-geochemical gradients via high-resolution numerical algorithms; and 3) inclusion of minerals such as calcite and Fe-minerals to control biogeochemistry and pH.

References

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Rates of Tc reduction by biogenic Fe(II) in subsurface sediment

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Technetium-99 is an important contaminant at many Department of Energy sites in the United States because of its long half life ($t^{1/2} = 2.13 \times 10^5$ y) and mobility in groundwater as the pertechnetate anion [Tc(VII)O₄⁻]. Pertechnetate can be immobilized, however, by reduction to insoluble Tc(IV)O₂•nH₂O at "intermediate" environmental redox conditions. Fe(II) resulting from the activity of dissimilatory iron-reducing bacteria (DIRB) is a particularly good, biogeochemical reductant for Tc(VII). Recent experimental data indicates that this reaction can proceed even in the high nitrate waters found in Hanford and Oak Ridge sediment.

Data collected to date indicate that the reduction kinetics depended in a complex manner on the biogenic Fe(II) concentration produced by DIRB and its molecular and mineralogic environment in the sediment. Biogenic Fe(II) in a "green rust-like" compound produced higher rates of reduction than Fe(II) surface complexes on Fe(III) oxides or layer silicates. For a given sorbed form (adsorbed or precipitated), the reaction was first-order with respect to sorbed Fe(II).

Column experiments provide quantification of the rates of Tc reduction at higher (and more realistic) sediment:solution ratios and under conditions of continuous low-level Tc(VII) supply and advective Fe(II) removal. A coupled biogeochemical transport model is used to extract *in situ* reduction (Tc(VII)/oxidation (Fe(II)) rates from these column transport experiments and these rates are compared with those obtained from batch experiments.

Mineral surface characterization of adsorbed and precipitated phases is used to develop a biogeochemical transport model with evolving phase reactivity. For example, the modeling will rely on direct measurements of Fe(II)/Fe(III) speciation and mineral form by Mössbauer spectroscopy and other techniques, and estimated properties of the Tc(IV)O₂•nH₂O phase association (e.g., size and surface area) made by XRM and scanning and transmission electron microscopy.