Scale Effects on Apparent Reaction Kinetics at the Oak Ridge FRC

Fan Zhang[1], Jack Parker[1], Phil Jardine[1], Melanie Mayes[1],
Tonia Mehlhorn[1], Jing-Ping Guo[2], and Scott Cesar[1]

[1]Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[2]Department of Civil & Environmental Engineering, University of Maryland, Baltimore, MD 21250

It is well known that hydrodynamic dispersion and physical mass transfer coefficients exhibit scale-dependence due to increases in fluid velocity variance that commonly occur with increased observation (averaging) scale. We hypothesize generally that reactive transport processes at different scales can be described by scale-independent mathematical formulations with scale-dependent coefficient values or functions. More particularly, we hypothesize that kinetic coefficients for reactions occurring in heterogeneous media will exhibit apparent scale-dependence due to smaller scale variability in fluid velocity, physical nonequilibrium limitations, reactive site densities and other media properties. We also hypothesize that uncertainty in apparent kinetic rates will increase with scale, due to higher local scale variability.

Studies of reaction kinetics and transport have been performed at various scale on soils at the Oak Ridge FRC and nearby sites with similar geology over a number of years undertaken through NABIR, EMSP and other programs. Experiments have involved Co-EDTA, Cd-EDTA, Cr and U reactions in batch systems, small disturbed cores, undisturbed cores of various sizes and field experiments. In this study, we focus on experiments involving Co(II/III)-EDTA as the data sets are more comprehensive and the reactions are fairly well-characterized. A conceptual model for Co(II)-EDTA and Co(III)-EDTA reactions with Oak Ridge soil material was developed that considers equilibrium ion-exchange and pH buffering reactions, kinetically-controlled redox reactions of adsorbed Co, and mass transfer reactions. The conceptual model was implemented numerically using the code HYDROGEOCHEM 5.0, which was coupled with the inverse solution module PEST to allow estimation of unknown model parameters (e.g., Gaines-Thomas coefficients, equilibrium constants, reaction rate coefficients, etc.) and their covariances by nonlinear regressions to experimental data. Uncertainty in model predictions, as quantified by deviations between model predictions and observations is evaluated to assess scale-dependence of model uncertainty.