

**B31F MCC: 3002 Wednesday  
1020h**

**Modeling Coupled Biogeochemical Cycles in Natural and Contaminated Systems: Linking Hydrogeological, Microbiological, and Geochemical Processes I** (*joint with H, OS*)

**Presiding: J T McGuire**, Texas A&M University; **E Roden**, University of Alabama

**B31F-01 1020h INVITED**

**Coupled modeling of transport and biogeochemical processes in aquifers - Model requirements, strength and limitations**

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Microbially mediated geochemical changes in aquifers may trigger a series of secondary reactions that include aqueous and surface complexation, ion exchange, and mineral dissolution-precipitation. Due to the coupled nature and the multitude of processes involved it is often difficult to identify the reactions controlling the system's overall evolution. Numerical models can be a useful component for identifying gaps and inconsistencies in conceptual models and for performing a more quantitative investigation of these systems.

Suitable computer codes must allow for a general description of transport and reaction processes to facilitate the investigation of site-specific conditions. In recent years significant advances have been made in terms of model generality and applicability. Major advances include the consideration of mass balance equations for reactants and reaction products, the integration of biodegradation and thermodynamic models, and the development of novel approaches for simulating biogeochemical processes and reactive transport under variably saturated conditions.

MIN3P is one of the codes capable of simulating coupled biogeochemical and hydrological processes on an increasingly mechanistic level. The simulation of column experiments and a hypothetical case study at the field scale illustrate how reactive transport modeling can be used. Modeling column experiments can be particularly fruitful, because detailed data can be collected to support the mechanistic approach. However, analysis of conceptual models is also beneficial on the field scale. The case study considered here describes natural attenuation of a petroleum hydrocarbon spill in an unconfined aquifer by multiple electron acceptors. The simulations also consider geochemical reactions triggered by contaminant degradation including the re-oxidation of reaction products during transport away from the source area. Comparing the results to contaminant plumes described in the literature suggests that geochemical trends can be described well for most reactants and reaction products. However, this would not have been possible without considering re-oxidation reactions. Remaining discrepancies with observed plumes suggest that mixing occurs between mobile plume water and stagnant background water along the flow path away from the source area. Simulations that make use of a dual porosity formulation provide a more realistic evolution of the concentrations of components such as O<sub>2</sub>, Fe(II) and CH<sub>4</sub>. The example is also useful in highlighting some of the model limitations, which include extensive data requirements to provide model constraints and non-unique results for components involved in several reactions.

**B31F-02 1035h**

**Integrating Hydrogeological, Microbiological, and Geochemical Data Using a Multi-Component Reactive Transport Model: Quantifying the Biogeochemical Evolution of Redox Zones in a Contaminated Aquifer**

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Hydrogeological, microbiological, and geochemical processes operating in a shallow sandy aquifer contaminated by waste fuels and chlorinated solvents were integrated using high-resolution mechanistic models. A 3-D, transient, reactive transport model was developed to quantitatively describe coupled processes via thermodynamic and kinetic arguments. The model was created by linking the hydrodynamic model MODFLOW (McDonald and Harbaugh, 1988), with advection, dispersion and user defined kinetic reactions based on RT3D 2.0. (Clement and Jones, 1998) and geochemical model PHREEQC (Parkhurst and Appelo, 1999). This model, BGTK3D 2.0, describes 1) the biodegradation of organic matter based on the influence of transport processes on microbial growth, 2) the complex suite of biogeochemical reactions operating in the aquifer, and 3) sharp chemical gradients. Some key features of this model are an ability to incorporate realistic solid phases to test hypotheses regarding mineral-water interactions, and an ability to accurately describe small-scale biogeochemical cycling (cm variability) observed in the field without oscillations or excessive numerical damping. BGTK3D was used to test hypotheses regarding the evolution of redox chemistry in a contaminated aquifer. The conceptual model that terminal electron accepting processes (TEAPs) distribute themselves sequentially into redox zones down flow path in aqueous systems is often used to interpret how and at what rates organic compounds will be degraded in the environment. Geochemical and microbiological data collected from a mixed contaminant plume at the former Wurtsmith AFB in Oscoda, Michigan suggests that under steady-state, mature plume conditions, traditional redox zonation may not be a realistic model of the distribution of TEAPs and therefore may not be the best model to evaluate the potential degradation of organic compounds. Based on these data, a conceptual model of TEAP evolution in contaminated systems was established. This model proposes that during initial plume development terminal electron acceptors O<sub>2</sub>, Fe<sup>3+</sup>, NO<sub>3</sub>, and SO<sub>4</sub>, are consumed sequentially based on thermodynamic arguments until a balance between organic degradation rates and source inputs 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 TEAs from all sides. Under these conditions, TEAPs will not proceed sequentially.

**B31F-03 1050h**

**Effect of Porous Media Particle Size on Bacterial Motility and Chemotaxis**

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Many soil-inhabiting bacteria that degrade chemical contaminants are both motile and chemotactic. Chemotaxis refers to the ability of bacteria to sense pollutant concentration gradients in water and preferentially swim toward regions of high pollutant concentration, and is thought to be important in guiding subsurface microbial populations toward chemical contaminants. Bacterial motion consists of a series of smooth-swimming runs interrupted by changes in direction. In the presence of a chemical gradient, bacteria bias their frequency of changing direction and demonstrate longer run lengths in the direction of increasing attractant concentration. One concern when studying bacterial chemotaxis in porous media is that in small pores, the porous media may interrupt the extended run lengths of bacteria swimming in the direction of a positive chemical gradient. The purpose of this study is to examine how a decrease in particle size affects the motility and chemotactic response of bacteria traveling through porous media. We employ an innovative technique for noninvasive visualization of changes in bacterial density distributions in a packed column as a function of time. Paramagnetic magnetite particles are attached to the surface of *Pseudomonas putida* F1 cells using an antibody. Bacterial distributions within a column of glass-coated polystyrene beads are imaged using magnetic resonance imaging (MRI), with a spatial resolution of 300 μm. Experiments are conducted with both 250-300 μm beads and 90-150 μm beads. Bacteria labeled with magnetite are introduced into a

specially designed chromatography column packed with glass-coated polystyrene beads. Bacterial migration is monitored over time using MRI, with and without the presence of a chemical gradient of trichloroethylene (TCE). Comparisons of the motility and chemotactic transport coefficients for *Pseudomonas putida* F1 cells traveling through different-sized samples of porous media in the presence of TCE will be presented and discussed. Results suggest a decrease in both motility and chemotaxis in the smaller-sized porous media.

**B31F-04 1105h**

**Modeling 3-D Coupled Variably Saturated Flow, Reactive Biogeochemical Transport, and Heat Transfer under Complex and Mixed Reaction Systems**

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A three dimensional numerical model HYDRO-GEOCHEM 5.0 has been developed to study the coupled variably saturated subsurface flow, reactive biogeochemical transport, and heat transfer under complex (multiple reaction types, including aqueous complexation, adsorption-desorption, ion-exchange, redox, precipitation-dissolution, and acid-base reaction) and mixed (equilibrium and kinetic) reaction systems. Theoretical bases and numerical implementations are summarized and three designed examples are presented. An complicated but realistic advective-dispersive-reactive transport problem is concerned in Example 1, in which three different schemes are compared in solving the governing transport equation: (1) FEM (Finite Element Method) on advective form; (2) Hybrid Lagrangian-Eulerian FEM for interior elements plus FEM on advective form for boundary elements; (3) Hybrid Lagrangian-Eulerian FEM. Example 2 focuses on employing different approaches to couple hydrologic transport and biogeochemical reactions: (1) Fully implicit iteration approach; (2) operator splitting approach; and (3) predictor-corrector approach. Example 3 is designed to explore the significance of the heat transfer on reactive chemical transport. This example will demonstrate how temperature affects the chemical transport as a consequence of changing the equilibrium constants; also in this example is the comparison of the simulation results under different heat transfer conditions. Keywords: Numerical Model; Groundwater; Reactive chemical transport; Heat transfer

**B31F-05 1120h**

**Assessing the effect of natural attenuation on oxygen consumption processes in a sewage-contaminated aquifer by use of a natural-gradient tracer test**

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Processes associated with aquifer restoration subsequent to cessation of treated-sewage loading in a sand and gravel aquifer are being investigated at the USGS Toxic Substances Hydrology Site on Cape Cod, MA. Restoration has been slow because of significant oxygen depletion resulting from biogeochemical processes associated with residual sorbed pools of organic carbon, ammonium, and reduced metals in the aquifer. The in situ interaction of the physical, chemical, and biological processes governing oxygen consumption was examined by using a natural-gradient tracer test in fall 2001, 6 years after sewage disposal had been discontinued. Ground water with a high dissolved oxygen (DO) concentration was withdrawn from an uncontaminated zone of the aquifer and re-injected with a conservative

tracer, bromide, into an anoxic zone directly below a former sewage-effluent disposal bed where Fe and sulfide concentrations were below detection and the DO was less than 5  $\mu\text{M}$ . An injection with negligible ammonium, a nitrate concentration of 22  $\mu\text{M}$ , and DO of approximately 260  $\mu\text{M}$  was maintained at approximately 15 L/hr for a period of 75 days. An array of multi-level samplers (MLS), placed at distances ranging from 1 to 7 m down-gradient from the injection well, was sampled prior to and throughout the 75-day injection, and during a 25-day period after the injection. Water samples from the MLS were analyzed for DO and a variety of aqueous constituents. The DO decreased from approximately 260  $\mu\text{M}$  to 210  $\mu\text{M}$  over 7 m of transport, indicating the presence of rate-limited oxygen consumption. An increase in nitrate from 22 to approximately 36  $\mu\text{M}$  indicated the presence of rate-limited ammonium oxidation. However, this ammonium oxidation was not sufficient to account for all of the DO consumption. Further characterization of these processes was accomplished by use of PHREEQC, a one-dimensional, geochemical reactive transport model. The 1D model is based on an ion association model for aqueous speciation. Surface complexation reactions were used to define the speciation for surface-complexed species, including ammonium and major cations. Kinetic reactions were defined for oxidation of ammonium and aerobic respiration of sorbed organic carbon. The initial chemical condition was specified as an equilibrium between a background solution, determined by using field data, and the surface sites, while flow was specified with constant flux boundary conditions on the basis of a steady-state injection. The model was calibrated by adjusting equilibrium constants and matching simulations to breakthrough curves observed in the tracer test at several distances downstream of the injection along the plume centerline. Modeling of breakthrough curves at different MLS ports suggested that aquifer heterogeneity and variability in the injection affected the geochemical reactions to some extent. Model simulations indicated that consideration of both aerobic respiration and ammonium oxidation was necessary to account for the observed oxygen consumption. This result, which was consistent with bacteria and dissolved carbon data, demonstrates that aerobic respiration and ammonium oxidation are important processes to consider when modeling the aerobic restoration of anaerobic, sewage-contaminated aquifers.

### B31F-06 1135h INVITED

#### Multi-Component Reactive Transport Modeling of Field-Scale Bioremediation: The Schoolcraft Site

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This paper describes three-dimensional multi-component reactive transport modeling for bioremediation of a carbon tetrachloride (CT) contaminated plume at the Schoolcraft site in Western Michigan. The denitrifying bacterium *Pseudomonas Stutzeri* Strain KC is used to mediate catabolic reactions that degrade CT to harmless end products. CT contamination at this site occurred due its use in the past as a fumigant in grain silos. The goal of the field bioremediation design was to inoculate a transect perpendicular to the natural gradient flow of a CT plume with microbes that could effectively remediate the CT contamination through a series of pulsed nutrient injections. The final design consisted of fifteen wells spaced one meter apart in which each well can operate either as an injection or an extraction well depending on the event. This design allowed us to operate in a semi-passive mode of operation with only 6 hours of pumping per week. Our modeling approach integrates information from laboratory-scale studies aimed at understanding the relevant rates and processes under controlled conditions with plume-scale modeling in the presence of a high degree of hydraulic control and significant heterogeneity to delineate the important differences in processes/rates as we proceed from the laboratory to the field. We describe the development of a seven component reactive transport model that includes the transport of aqueous and sorbed-phase CT, mobile and immobile bacteria, acetate (electron donor), nitrate (electron acceptor) and tracer (bromide) and show detailed comparisons of observed and simulated concentrations at a number of wells and at different depths. Processes simulated in the model include advection, dispersion, degradation, two-site sorption, microbial attachment, detachment, growth and decay. We describe the influence of several modeling decisions (e.g., effects of dynamic partitioning, bioavailability and sorption) on the predictions of the model. Most parameters in the reactive transport model were fixed based on earlier laboratory ex-

periments and literature values and only a few parameters were changed due to the likelihood of differences between the laboratory and field. The computational model used a non-uniform grid with very fine cells placed around the delivery well gallery to better resolve the gradients. We present the spatial-temporal evolution of the degradation front and the microbial concentration fields and demonstrate how high-resolution numerical models can be used to aid our understanding of complicated field-scale processes.

### B31F-07 1150h

#### Modeling Biogeochemical Reactive Transport in Fractured Granites: Implications for the Performance of a Deep Geological Repository

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Several countries around the world are considering deep repositories in fractured granitic formations for the final disposal of high-level radioactive waste. Evaluating the long term safety of such repositories requires sound conceptual and numerical models which are being developed from data and knowledge gained from in situ experiments carried out at deep underground laboratories such as that of spö in Sweden. One of the key aspects for performance assessment concerns to groundwater redox conditions because: (a) the presence of oxygen will affect to the corrosion of canisters, (b) possible production of hydrogen sulphide from sulphate reduction will also have a negative effect on these metallic containers, and (c) several long-lived radionuclides are much more soluble and mobile under oxidizing conditions. Several projects have been performed at spö to investigate different aspects of the groundwater redox evolution. The vast amount of in situ-generated information has been used in this work to set up coupled hydrobiogeochemical models. Numerical models account for saturated groundwater flow, solute transport by advection, dispersion and molecular diffusion, geochemical reactions involving both the liquid and solid phases, and microbially-catalyzed processes. For the spö site, modelling results provide quantitative support for the following conclusions. (A) At the operational phase of the repository, shallow fresh groundwater could reach the depth of the underground facility. Shallow groundwaters loose dissolved oxygen during the infiltration through soil layers and then, respiration of dissolved organic matter is induced along the flow paths through the reduction of Fe(III)-bearing minerals of the fracture zones. Microbial anaerobic respiration of DOC provides additional reducing capacity at the depth of the tunnel. (B) After repository closure, atmospheric oxygen will remain trapped within the tunnel. Abiotic consumption of this oxygen has been computed to occur in a period of about 1,000 years as a result of diffusion-reaction processes. Coupled biogeochemical mechanisms, such as respiration of dissolved organic matter and aerobic methane oxidation, accelerate the oxygen uptake to less than a month.

### B31F-08 1205h

#### Rare Earth Element - Humic Acid Interaction: Experimental Evidence for Kinetic and Equilibrium Fractionation in Aqueous Systems.

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Dissolved organic matter (DOM) is well known for its strong binding capacity for trace metals. In order to better predict the role of DOM in the speciation and transport of trace metals in the environment we coupled capillary electrophoresis (CE), a molecular separation technique, to a Sector Field Inductively Coupled

Plasma Mass Spectrometer (SF-ICP-MS). The combination of these two techniques allows for the study of non-labile metal speciation in aquatic samples. By separating Rare Earth Element (REE) complexes with EDTA and Humic Acid's (i.e. ligand competition) we have been able to determine conditional equilibrium binding constants (Kc) and kinetic rate constants for all 14 REE's with Humic (HA) and Fulvic Acids (FA) as a function of pH (6-9) and ionic strength (IS, 0.01-0.1 mol/L). Assuming a 1:1 binding mechanism, logKc values for REE-FA varied from 9.0 (La) to 10.5 (Lu) at pH 6, 0.1 mol/L IS, and 11.7 (La) to 14.6 (Lu) at pH 9, 0.1 mol/L IS. LogKc values for REE-HA were 10.6 (La) to 12.2 (Lu) at pH 6, 0.1 mol/L IS and 13.2 (La) to 16.5 (Lu) at pH 9, 0.1 mol/L IS. Slightly higher values for Kc were obtained at 0.01 mol/L IS. The general observations of stronger REE-HA binding compared to REE-FA, and stronger binding with increasing pH and decreasing IS correlate with our current understanding of metal-DOM interactions (1). Both Kc's as well as kinetic rate constants increase with increasing REE mass number (decreasing ionic radius); a reflection of the well-known lanthanide contraction. This is the first comprehensive metal binding dataset between REE and DOM, and the first experimental evidence for differential equilibrium and kinetic binding behavior between REE's and DOM. The 30-1000 fold increase in binding strength of heavy REE's with DOM provides for an equilibrium fractionation mechanism that may explain features of the global geochemical REE cycle such as fractionation related to weathering, estuarine mixing, and REE scavenging in the deep ocean (2). The experimental dataset has also been interpreted with the Non-Ideal Competitive Adsorption - Donnan (NICA-Donnan (1)) model for HA and FA metal binding, such that REE-HA binding can be predicted as a function of pH and IS. The NICA-Donnan model is a standard object in the novel object oriented chemical speciation code ORCHESTRA (Objects Representing Chemical Speciation and Transport (3)) that we used to explore the possible effects of pH and IS on fractionating the REE's along an estuarine gradient.

(1) Milne, C. J.; Kinniburgh, D. G.; Van Riemsdijk, W. H.; Tipping, E. *Environmental Science & Technology* 2003, 37, 958-971. (2) Elderfield, H.; Upstill-Goddard, R.; Sholkovitz, E. R. *Geochimica Et Cosmochimica Acta* 1990, 54, 971-991. (3) Meeussen, J. C. L. *Environmental Science & Technology* 2003, 37, 1175-1182.

### B31G MCC: 3014 Wednesday 1020h

#### Ecosystem Interactions with Land-use Change II (joint with H)

Presiding: G P Asner, Carnegie

Institution; R DeFries, University of Maryland

### B31G-01 1020h INVITED

#### The Conservation Value of Human-Dominated Countryside

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The future of biodiversity and the benefits it supplies society depend largely on the conservation value of human-dominated 'countryside,' the growing fraction of Earth's unbuilt land surface whose ecosystem qualities are strongly influenced by humanity. I will report on the conservation value of tropical countryside for a variety of groups of organisms and ecosystem services. The work is based on species distributions and dynamics; remote sensing, radio telemetry, and GIS; and assessments of the ecosystem functions performed by diverse organisms. While conservation value appears high today in regions under low- and intermediate land-use intensity, the window of opportunity for securing this value is closing rapidly with on-going intensification of land use.

### B31G-02 1040h

#### On the Impact of Historical Land-use Changes on the Summer Climate of a Swiss Region

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In the second half of the 19th century a major civil engineering project was initiated to adjust the lake