NABIR Modeling Working Group
Semi-annual Report
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The goal of the NABIR Modeling Working Group is to facilitate efforts aimed at development of a comprehensive framework for modeling complex hydrobiogeochemical behavior in subsurface media across relevant observation scales. The following summary of NABIR modeling efforts performed in the last half year was edited by Jack C. Parker, Group Leader, based on information provided by group members.

Roden and Scheibe (2005) reported a conceptual model and numerical simulations of bacterial U(VI) reduction in fractured subsurface sediments to assess the feasibility of biomineralization at the fracture-matrix interface as a mechanism for uranium immobilization. The model envisions flow of anaerobic groundwater with or without acetate as an electron donor for stimulation of U(VI) reduction by dissimilatory metal-reducing bacteria (DMRB) within mobile macropore regions. As groundwater moves along the flow path, U(VI) trapped in immobile mesopore and micropore domains becomes desorbed and transferred to the mobile macropore zone via a first-order mass transfer process. By allowing bacterial U(VI) reduction to occur in the mesopore domain (assumed to account for 12% of the total sediment pore volume), using experimentally-determined kinetic parameters and an assumed DMRB mass of 10^7 cells per cm^3 bulk sediment, the concentration of U(VI) in the macropore domain was predicted to be reduced ca. 10-fold compared to that in the absence of mesopore DMBR activity after a 6-monthperiod. The results suggest that input of soluble electron donors over a period of years could lead to a major redistribution of U in fractured sediments, converting potentially mobile sorbed U(VI) to an insoluble reduced phase (uranite) in the mesopore region that could be permanently immobilized if anaerobic conditions were sustained.

Roden, Fang, Scheibe and Brooks (2005) developed and tested a numerical model involving a suite of aqueous and solid phase geochemical reactions and microbially-mediated redox reactions for multiple terminal electron acceptor processes (TEAPs) including soluble oxygen, nitrate, U(VI) and sulfate and solid-phase manganese and iron oxides and sulfur. The model considers a batch reactor with aqueous ethanol and electron acceptors (O_2, NO_3^-, SO_4^{2-}) whose abundance, together with the abundance of solid-phase electron acceptors (MnO_2 FeOOH, S) in the sediment, control relative rates of various TEAP and other biogeochemical reactions. The model accounts for complete (to HCO_3^-) or incomplete (to acetate) oxidation of ethanol, as well as oxidation of acetate to HCO_3^- and/or CH_4, via 18 different TEAP pathways. Each of the TEAP reactions are dependent on the biomass of one or more of eight distinct microbial populations chosen based on current knowledge of the kinds of organisms likely to proliferate in response to biostimulation of subsurface sediments. Growth of these populations is described using the bioenergetics-based approach developed by Rittman and McCarty (2001) for simulation of wastewater treatment, in which the partitioning of organic carbon flow between energy generation and cell biomass production is dependent on the free energy of the corresponding TEAP, which is computed dynamically during the simulation as a function of the abundance of reactants and products involved in the process. This approach alleviates the need for making a priori assumptions about the biomass yield for the different physiological functional populations. Kinetic constants for uptake of electron donors, electron acceptors, and inorganic nitrogen compounds, as well for the inhibition of specific TEAPs (37 total) by the presence of more favorable electron acceptors, were either chosen arbitrarily or constrained by the

physiological properties of pure culture representatives and/or by values required to reproduce the results of the batch slurry experiment. Each of the TEAPs results in production of various inorganic compounds, which either accumulate in solution or undergo reactions (sorption and/or mineral precipitation) with the solid-phase. The model also accounts for a wide variety of secondary redox reactions that may occur in sedimentary environments (e.g. oxidation of reduced species such as Mn(II), Fe(II), U(IV), S(-II), S^0, and CH_4 by aqueous or solid-phase electron acceptors such as O_2, NO_3^-, MnO_2, and FeOOH, as well as for precipitation/dissolution of mineral phases that may be associated with microbial activity in sediments. In this way, the model is capable of simulating time-dependent changes in the abundance of various oxidized and reduced species and mineral phases as a function of the input of external electron acceptors/donors and other aqueous species.

The model is currently programmed as a standalone computational module, but it is planned to convert the reaction network to system of equations that can be input into the reactive transport model HYDROGEOCHEM vers. 5 (Yeh et al., 2004) for field-scale modeling of subsurface biostimulation at FRC Area 2.

Arrays of both batch and column experiments on iron bioreduction were conducted with lactate as electron donors using natural sediment material obtained from Area 2 of the NABIR Field Research Center. A reaction network was proposed to describe the experiments, which consists of several biogeochemical processes including dissimilatory iron reduction for energy production, cellular synthesis, hydration, abiotic sorption of biogenic ferrous iron, and PIPE buffering.

Yeh, Burgos and colleagues performed modeling studies of bath and column experimental data. Two different rate formulations were considered to describe energy production reactions. Results indicated that both formulations can adequately simulate batch and column measurements. Furthermore, simulations demonstrated that batch models can be upscaled to column models if the former are iteratively formulated with the later (Yu, et al, 2004). For example, in a batch model, equilibrium formulations for some of the reaction networks are sufficient, but these equilibrium formulations have to be modified with kinetic formulations in column modeling (Yu, et al., 2004). After the column model was complete, the batch model was then revisited and refined with the same kinetic formulations but with slightly different reaction parameters. This illustrated that scale-invariant rate formulations can be obtained iteratively between two scales.

To further improve the modeling, one additional rate formulation was proposed for the energy production reaction (Chen, 2005). This rate equation is based on a dual Monod kinetics modified with ferrous iron inhibition. The biosynthesis reaction is described by Monod kinetics modified with decay of biomass. Preliminary results showed that these optional rate formulations improve simulations in both batch and column experiments (Chen, 2005). Especially, for column experiments, the simulations are greatly improved with the optional rate equations. Further research for better, mechanistically-based rate formulations may be needed.

As more complex biogeochemical situations are being investigated (e.g., evolving reactivity, passivation of reactive surfaces, dissolution of sorbates), there is a growing need for biogeochemical simulators to flexibly and facilely address new reaction forms and rate laws. An approach was developed that accommodates this need to efficiently simulate general

biogeochemical processes, while insulating the user from additional code modification (Fang et al., 2005). Future modeling efforts will focus on the developments and numerical simulations of reaction networks and the formulation of reaction rates that can better and further elucidate the mechanisms of Fe(III) oxide reduction, biosynthesis, abiotic geochemical processes, and coupled Fe(III) oxide/U(VI) reduction in sediments at the NABIR field research center.

Efforts to implement a site-wide model of the FRC and to coordinate this effort with individual FRC-based projects continued during the last six months. Refinements of the site-wide groundwater flow model were made to incorporate new field data and additional refinements are planned to accommodate more recent field investigations in fill and rock-saprolite transition zones, which are expected to affect shallow flow and transport paths. A geochemical reaction network was incorporated into HYDROGEOCHEM vers. 5 and successfully tested against laboratory batch and column experimental data and a preliminary field-scale transport simulation was performed with the geochemical reaction network (Zhang et al., 2005).

Efforts are in progress to utilize the site-wide model to provide information on site hydrologic properties and groundwater velocities to NABIR research groups at PNNL, Oregon State and Stanford in order to expedite field plot-scale modeling efforts. Simulations with the site-wide model are planned to help guide additional field-characterization studies planned over the next several months.

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