

Incorporating geomicrobial processes in subsurface reactive transport models

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The chemical structure and evolution of subsurface environments is to a large degree determined by the activity of the resident microbial populations (Chapelle, 2001). In particular, the distributions of redox-sensitive constituents are strongly affected by microbial metabolism, as electron transfer processes form the basis of biological energy generation. However, microbial reactions also modify acid-base and electrolyte properties of pore waters, thermodynamic driving forces, and the composition of particulate and colloidal matter in soils, sediments and aquifers. Comprehensive subsurface reactive transport modeling therefore requires mathematical expressions that predict the rates at which microbial populations consume and produce chemical constituents.

When representing microbial reaction processes in reactive transport models it is commonly assumed that microorganisms exhibit saturation kinetics with respect to the substrates they extract from their surroundings (e.g., Curtis, 2003). That is, with increasing concentration of a limiting substrate, the reaction rate ultimately reaches a maximum value. This behavior is captured by the so-called Michaelis-Menten (or Monod) rate expression. Michaelis-Menten kinetics, however, have mainly been verified for pure cultures utilizing soluble substrates. We present the results of a number of experimental studies, which confirm that the Michaelis-Menten formulation also holds for redox transformation processes carried out by complex, natural microbial communities. In addition, we show that the utilization of solid-phase Fe(III) substrates by pure cultures of iron reducing bacteria follows Michaelis-Menten saturation kinetics (Bonneville et al., 2004).

The accumulating empirical evidence therefore confirms that the Michaelis-Menten equation provides a generally valid description of the utilization of external substrates by microorganisms. Hence, it forms the logical starting point for the development of mathematical representations of geomicrobial processes in reactive transport models. We present an extended Michaelis-Menten model, which accounts for multiple substrates, changes in the microbial community structure, the presence of inhibitors, and the free energy yield of the microbial reaction pathways. Two applications of the extended Michaelis-Menten model are discussed.

In the first application, we analyze the order of utilization of terminal electron acceptors during the anaerobic degradation of sedimentary organic matter. The simulations show

that competition between the organic carbon oxidation pathways depends in the first place on the values of the affinity constants for the electron donors and, to a lesser degree, on the growth yields of the heterotrophic microbial populations. However, they further indicate that, when labile organic matter is abundant, the affinity constants for the electron acceptors also play an important role in the reaction dynamics. In particular, these affinity constants influence the relative distribution of TEA utilization over competing reduction pathways. For example, a decrease in the affinity constant of Fe(III) (hydr)oxides for iron reducing bacteria may shift Fe(III) reduction to reaction with sulfide, which consequently promotes organic matter degradation by sulfate reducing bacteria. Furthermore, with increasing availability of labile organic matter, there is growing spatial and temporal overlap among respiratory pathways using different TEAs. This theoretical result agrees with recent experimental studies (e.g., Koretsky et al., 2003).

In the second application of the extended Michaelis-Menten model, we consider the anaerobic oxidation of methane by sulfate (AOM), a geomicrobial reaction system operating close to its thermodynamic limit (e.g., Hoehler et al., 1994). The consortia of methane oxidizing archaea and sulfate reducing bacteria carrying out AOM depend on a close syntrophic association and energy sharing for their survival. In particular, the sulfate reducers are essential for the disposal of H₂ produced by the methane oxidizers. To simulate the activity of these microbes, as well as the turnover of methane at the seafloor, we have developed a reaction network model including methane oxidation and sulfate reduction coupled to H₂ oxidation, as well as methanogenesis, acetogenesis, fermentation, and sulfate reduction coupled to oxidation of organic fermentation products.

Our current reaction network model embodies the still fragmentary conceptual understanding of how AOM communities function. Yet the model already requires over 40 independent parameters. This large number of parameters reflects the inherently complex nature of reaction systems in which multiple microbial groups participate. To identify those parameters, or combination of parameters, that most significantly affect the model output, we use a two-level factorial analysis. A baseline, or nominal, simulation is first conducted, using the best available estimates of the parameters. Subsequently, perturbations are carried on groups of two or more parameters and the deviation from the nominal run of some defined model response is monitored (Montgomery, 1997). The sensitivity range for each parameter is chosen based on experimental data or informed guesswork.

Using a nominal coastal sediment scenario, the most sensitive parameters for AOM are found to be those belonging to sulfate reduction coupled to H₂ oxidation and methane production from acetate. In particular, the model response is sensitive to the Gibbs energies of reaction of the two pathways. The latter observation reinforces the importance of including thermodynamic constraints in the kinetic descriptions of the metabolic pathways in the reaction network. The sensitivity analysis further shows that the overall rate of AOM is not sensitive to the kinetic and thermodynamic parameters directly related to the methane oxidation pathway or the biomass of methane oxidizers. That is, the

explicit representation of these parameters, and the related variables, does not improve the performance of the reaction network model. This result, which at first may seem counterintuitive, would not have been obtained without considering the entire set of microbial pathways and their interactions.

As knowledge about microbial processes and their interactions expands, it becomes possible to develop increasingly detailed model representations of geomicrobial reaction systems. This, in turn, creates the need for robust approaches for parameter identification and calibration, as illustrated here for the case of AOM. Global sensitivity analyses, for example using factorial analysis, help identify those parameters that need to be targeted in future laboratory and field experiments. They further provide guidelines for the derivation and parameterization of simplified mathematical reaction models that can be incorporated in reactive transport codes. Therefore, the development of detailed biogeochemical reaction network models helps closing the gap between fundamental research in geochemistry, microbial ecology and molecular biology, and application-oriented reactive transport modeling.

References

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