Reactive transport modelling of microbially-driven redox chemistry: application to subsurface environments

K. S. Hunter
School of Earth & Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia 30332, USA

Y. Wang
Sandia National Laboratories, Carlsbad, NM 88220, USA

P. Van Cappellen
School of Earth & Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia 30332, USA

The complexity of multi-component, multi-reaction subsurface environments requires sophisticated models to realistically simulate the biogeochemical dynamics of these systems. Traditional geochemical modelling of groundwater composition has been based primarily on thermodynamic equilibrium calculations. While equilibrium-based models are sometimes able to reproduce field and laboratory observations pertaining to relatively fast inorganic reactions, they are not adequate to represent the irreversible microbial degradation of organic matter, secondary redox reactions, or mineral precipitation and dissolution reactions (Hunter *et al.*, 1998). Hence, kinetic models are needed for describing the reactions that drive the redox plus acid-base chemistry of groundwaters.

The biogeochemical dynamics of subsurface environments are characterized by complex reaction networks. Frequently, the product of one reaction acts as a reactant in one or more other reactions. Furthermore, parallel reactions often compete for the same chemical compounds. The competition may involve microbially-mediated reaction pathways, inorganic reactions, or both. Central to the redox chemistry of groundwaters is the microbially-mediated decomposition of organic compounds which results in the consumption of dissolved and solid oxidants (O_2, , Mn(III, IV), Fe(III),) and the production of reduced inorganic compounds (e.g. H_2S, Fe^{2+},). Reaction fronts may develop when the reduced species are transported to more oxidized areas and are subsequently reoxidized.

A fully kinetic, multi-component, reactive transport model is presented here. The model equations describe transport by flow and dispersion, and homogeneous plus heterogeneous reactions, including both inorganic and microbially-mediated reactions. In general, all the chemical species are involved in kinetically-controlled reactions, while only a subset of the species also participate in reactions that are sufficiently fast to remain in local equilibrium. Because the rate expressions incorporate the concentrations of multiple species, the reactive transport equations of the independent species are directly coupled to one another via the reaction rate terms. All of the reactions included in the model, with the exception of homogeneous complexation reactions and sorption processes, are kinetically-controlled.

When groundwater transporting dissolved organic compounds and reduced inorganic species reaches an aerobic zone, some of the oxidants will be consumed by secondary redox reactions (i.e. redox reactions not involving the oxidation of organic carbon), thereby reoxidizing the reduced inorganic species and leaving only a fraction of the oxidants available for use in the microbial respiratory pathways (i.e. aerobic respiration, denitrification, manganese reduction, iron reduction and sulphate reduction). To demonstrate this, a numerical simulation was done in which leachate from a landfill infiltrates into a previously pristine, aerobic aquifer.

In the simulation, reduced, organic-rich leachate is transported away from the source area, causing the aquifer to become anoxic within the boundaries of the plume. In the plume, the dissolved organic matter from the leachate is degraded via microbially-mediated pathways, resulting in the complete consumption of all available electron acceptors. At the downstream edge of the plume, the highly reduced porewaters come into contact with oxidized porewaters from the surrounding aquifer and a reaction front develops. There is significant competition between primary (i.e. microbial biodegradation) and secondary reaction pathways for the electron acceptors present at this interface. For example, the calculations reported in Table 1 predict that 90% of the O_2 and all of the supplied by the groundwater are diverted to the oxidation of reduced inorganic species carried by the contaminant plume. Similarly, large

TABLE. 1. Percentages of electron acceptors consumed by primary and secondary pathways in the downstream reaction front of a leachate plume

Primary pathways	O_2	Mn(IV)	Fe(III)	SO_4^{2-}
$C_{org} \rightarrow CO_2$	10	<1	78	0
Secondary pathways				
$Mn(II)_{aqueous} \rightarrow MnO_2$	25			
$Fe(II)_{aqueous} \rightarrow Fe(OH)_3$	18	89		
$H_2S \rightarrow SO_4^{2-}$	<1			
$H_2S \rightarrow S^0$		10	22	
$FeS \rightarrow SO_4^{2-}$	0			
$CH_4 \rightarrow CO_2$	46			100

fractions of the reactive Mn oxides and Fe hydroxides of the rock matrix (99% and 22%, respectively) are consumed by secondary reactions. At the reaction front, denitrification and iron reduction are the dominant pathways by which the organic carbon is oxidized, despite the availability of O_2. When the simulation was rerun without the inclusion of the secondary reactions, aerobic respiration became the dominant pathway, with both manganese and iron reduction also showing increases and denitrification being sharply reduced.

The relative amounts of the oxidants consumed by the different reaction pathways depends on the kinetics of the reactions involved, but it is clear that there is competitive interaction between the respiratory pathways which produce reduced inorganic compounds and the secondary reactions in which the latter are consumed (Hunter *et al.*, 1998). Hence, the spatio-temporal distribution of the organic matter degradation pathways not only depends on the availability of organic substrates and terminal electron acceptors, but it also depends on their coupling to the secondary reaction network. This is an important point which is often overlooked, both in modelling and in the interpretation of field data. Making the assumption that all of the oxidants are available for use in the degradation of organic matter may lead to erroneous interpretations of measured chemical distributions with regard to the sources and sinks of the individual chemical species. Similarly, not including a secondary reaction network when constructing numerical models will lead to incorrect predictions when analysing the potential for natural attenuation of organic compounds in subsurface environments. Additionally, by ignoring the secondary redox reactions, the build-up of reaction products (e.g. methane and sulphides) in the system may be predicted incorrectly.

References

Hunter, K.S., Wang, Y. and Van Cappellen, P. (1998) *J. Hydrol.*, in press.