

REDOX MICRO-NICHES, A MODEL STUDY OF THE VIABILITY OF SUB-GRAINSCALE GEOCHEMICAL HETEROGENEITIES FOR CREATING GROUNDWATER WITH IRON, SULFIDE AND METHANE

RASMUS JAKOBSEN¹

¹ *Environment & Resources DTU, Technical University of Denmark, Bygningstorvet, Building 115, DK-2800 Kgs. Lyngby, Denmark*

ABSTRACT

A pore-scale model using PHAST is set up to study to what extent inter- and intragranular micro-niches can affect the distribution and presence of redox processes and other geochemical processes in a groundwater system, and to what extent such local effects are impeded by diffusion. The model takes diffusive transport and advective transport into account but not the actual velocity distribution within the active flow channels. However using the features of PHREEQC, an integral part of PHAST, it is possible to implement a complete geochemistry, in this case including FeS precipitation, calcite dissolution and precipitation, as well as a partial equilibrium description of the redox processes; Fe-oxide reduction, sulfate reduction and reversible methanogenesis, implemented with a gap in the Gibbs energy where there is no reaction. The model result indicates that a separation of redox processes within the porespace is possible, given that the stagnant pores are deep enough, and that the organic matter is reactive enough. Assuming a finite energy requirement for the microbial reoxidation of methane, the common observation of methane in many aquifers that are not extremely reduced can be explained, but in most aquifers the organic matter reactivity will be so low that lumps of organic matter rather than intragranular coatings or fragments of organic matter are required. The model indicates that ongoing redox processes may lead to secondary processes, occurring at the grain-scale; e.g. the oxidation of organic matter in a micro-niche releases CO₂ which dissolves calcite, which is reprecipitated where the Fe-oxides are being reduced, due to the locally increased pH.

1. INTRODUCTION

It has been found that organic matter in sediments is often associated with very small, presumably intra-granular pores e.g. Mayer (1999), who described a proportionality between the surface area of the sediment and the amount of organic carbon in the sediment, indicating that the organic matter in the smallest micro-pores is perhaps protected from oxidation. However since redox processes also occur in these sediments there must be organic matter present which is able to react, and accordingly a much lower amount of organic matter per surface area has been found in aquifer sediments. The question is whether the organic matter reacting in aquifers is present in lumps of grain size, or whether it is present as inter- or intragranular coatings, in pores that are too large to protect the organic matter. This localized

organic matter could lead to a range of redox conditions on the grain or sub-grain-scale. Such micro-niches are often proposed as the cause for the observation of somewhat odd geochemical, especially redox compositions of groundwater sampled from aquifer systems. In many cases the most probable explanation for the odd geochemistry is that the intake of the well spans several redox zones, but in other cases intake screens are so small and set so far from transition zones that this seems improbable. The question is then, if the different redox zones are present as mm-cm size micro-volumes inside e.g. lumps of organic matter, or whether it is feasible for these micro-niches to be present on a sub-millimeter i.e. sub-grain-scale in the vicinity of reactive organic matter present in inter- or intragranular stagnant zones or whether diffusive transport, which is important over small distances, makes this impossible considering the low rates and thereby reactivity of organic matter observed in most aquifer systems. To take an example, will the rate of diffusion of e.g. the H_2 produced by one type of microorganism be so fast compared to the production, that the H_2 never builds up to a level necessary for the methanogenic bacteria to be able to obtain the threshold energy that they need.

Geochemical systems comprising redox processes in the form of microbiologically mediated terminal electron accepting processes (TEAP's) have been modelled in numerous ways recently described in: Brun and Engesgaard (2002), Curtis (2003), Thullner et al. (2005) and Watson et al. (2005). The approach taken here is based on a partial equilibrium approach as described in the following. Models of geochemical and biogeochemical processes at a pore scale, though with different focuspoint and a much more sophisticated modelling of the flow itself, has recently been published by e.g. Knutson et al., (2005) as well as Meile and Tuncay (2006).

2. MODEL SETUP AND RESULT

2.1 Model setup.

The model system used here is setup in PHAST (Parkhurst et al., 2005), a reactive transport model based on HST3D (Kipp, 1998) and PHREEQC (Parkhurst and Appelo, 1999) capable of 3D reactive transport in saturated media using a non-iterative split-operator scheme for solving the reactive transport problem. This implies that the solutions of all cells are transported the distance calculated by the flow model in a given time-step, and then the geochemical reactions going on between the solutions and the solid (or embedded gas) phases (kinetic reactions, equilibrium reactions, ion-exchange, surface complexation etc.) in the cells are made subsequently.

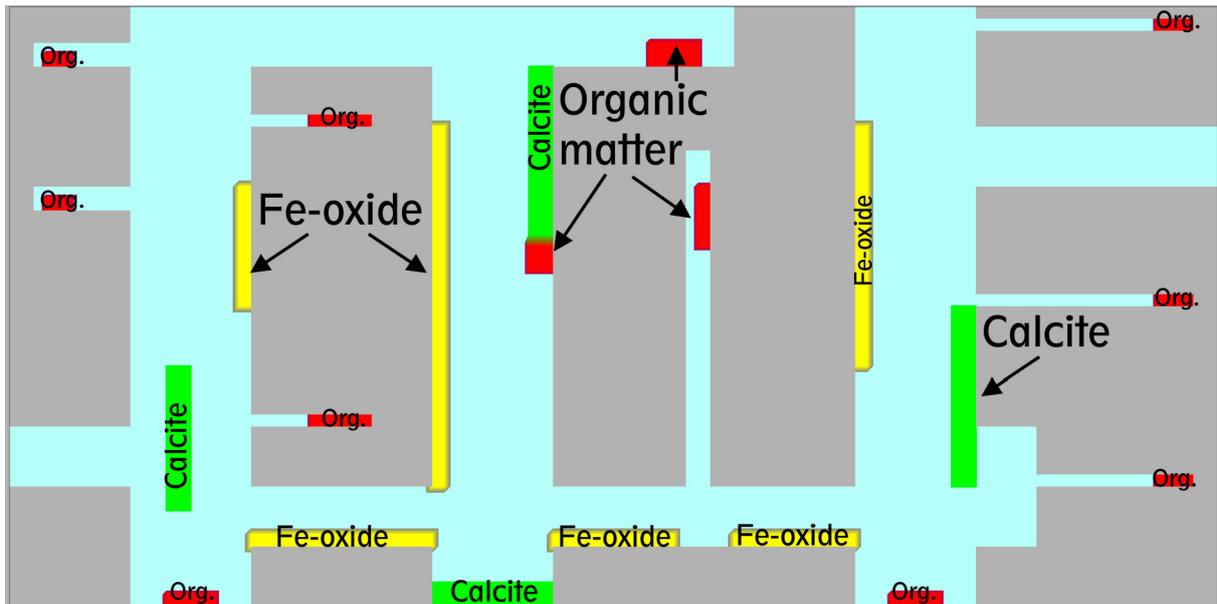


FIGURE 1. The 4x2 mm model domain showing the position of the Fe-oxide and calcite equilibrium phases and the organic matter added as a reactant at a rate controlling the rate of the TEAP's.

The model setup used here (Figure 1) is a 2D 4x2 mm grid discretized in 40 μ m square cells consisting of a very simple set of rectilinear channels, of which some are dead-end ones of varying depth, running between rectangular areas, “grains”, of the model with no flow as they are defined as inactive.

This leads to a model where the flow distribution is simply related to transmissivity, the velocity is a simple function of flux and cross-sectional area, and there is no parabolic velocity distribution in the channels. To introduce some sort of realism, the geochemistry and parameters controlling flow are adjusted so that the flow and velocity through the model is comparable to the Rømø aquifer described by Jakobsen (1999) and Hansen et al. (2001). Advective flow through the system is obtained by fixed head boundary conditions at the left and right side of the model domain with a gradient of 0.00165 as observed in the field on a macroscopic scale. There is no defined advective dispersion, and the solution method used is central in time and space to minimize numerical dispersion, to what may result from the split-operator scheme. The dispersion observed using 10 second time-steps is very small, but there are some numerical oscillations even though the 10 second time-steps imply that the solution is never moved more than 0.3 cell-lengths. However, when diffusion is added in with a diffusion coefficient of 3.0×10^{-10} m²/s these oscillations disappear and spreading due to diffusion is seen to be very significant. In view of the very low dispersion observed without diffusion it is assumed that when diffusion is active the modelled spreading of solutes in the model domain is a reasonable representation of diffusive spreading within the model and especially to and from the stagnant zones where the possible effect of a parabolic velocity distribution must be absent.

The flow rates were adjusted by changing the hydraulic conductivity in the active parts of the model domain. The solution used as both the initial solution and the solution flushing is a solution very close in composition to a measured solution from a level in the Rømø aquifer where direct sulfate rate measurements and changes in pore water chemistry over depth

indicate concomitant Fe-oxide reduction, sulfate reduction and methanogenesis. The solution composition is given in Table 1.

Table 1. The chemical composition of the solution used derived from a groundwater sample from the Rømø aquifer (Jakobsen, 1999)

Al	Alk.	CH ₄	Ca ^a	Cl	Fe(2)	Fe(3) ^b	K	Mg	Mn	Na	Sulfate	Sulfide ^c
mM	mM	mM	mM	mM	mM	μM	mM	mM	μM	mM	mM	μM
0.05	3.67	0.10	4.68	0.90	0.43	0.0053	0.09	0.19	6.0	0.57	0.17	0.91

^acalculated from equilibrium with calcite; ^bcalculated from equilibrium with Fe(OH)₃(a);

^ccalculated from an SI=1 for FeS(ppt)

Subdomains of the model are defined to either contain calcite, Fe-oxides or organic matter as shown in Figure 1. FeS is allowed to precipitate anywhere in the active model domain should the solution become super-saturated beyond a saturation index of one. Redox reactions occurring in the system are defined using the partial equilibrium approach (Postma and Jakobsen, 1996, Jakobsen and Postma, 1999). Organic matter is added to the system triggering irreversible reduction of in this case Fe-oxides, sulfate and CO₂. The approach is extended so that the reaction will only proceed if energy is available to the microorganisms presumably mediating the processes. This implies that the process will only proceed if the energy available is above a certain threshold, corresponding to a mineral not precipitating until a certain super-saturation is exceeded. These threshold energies are expressed in the observed steady-state H₂ level and are reasonably well-established for sulfate reduction and methanogenesis, though a considerable difference in the threshold energy can be observed when comparing systems and setups. To enable a comparison with observed threshold energies, the reactions are rewritten within PHREEQC so that H₂ rather than electrons figures as the electron donor. It has never been shown to what extent Fe-oxide reduction can be described as a partial equilibrium reaction, and due to the Fe-oxide being a solid-phase it may be an oversimplification. However as shown by Jakobsen and Postma (1999) it is possible to model the observed dissolved Fe(2) profiles using the approach. Methanogenesis is potentially a reversible process in this system, so in order to model this using the partial equilibrium approach, still ensuring that the microbiologically mediated methanogenesis or methane oxidation only occurs when the amount of energy is high enough, the kinetic feature of PHREEQC is used to calculate the energy available for the process and the amount of reaction necessary for the energy to reach the threshold for either process. So though the kinetic feature is used it is still a equilibrium reaction, with the difference that there is a gap in the Gibbs energy, in this case from -5 - +5 kJ/mole H₂ for reversible methanogenesis. The approach was applied by Jakobsen (2002) in a 1-D simulation with stagnant cells juxta-posed to cells with advection. The reactions and equilibria that can occur in the system given the solutions, equilibrium phases, and kinetic reactions are summarised in Table 2 with the threshold energies for the redox reactions entered into the model.

TABLE 2. The irreversible, equilibrium and redox reactions defined in the model and the Gibbs energy available for the microorganisms. organic matter is irreversibly added at the overall controlling rate, producing H₂ by the equilibrium reaction. This H₂ enters as reductant in the terminal electron acceptor reactions Fe(III) reduction, sulfate reduction and methanogenesis, or may be produced from methane by methane oxidation.

Reaction	Available Gibbs energy kJ/mol H ₂
$\text{CH}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{e}^- + 4\text{H}^+$	irreversible
$2\text{H}^+ + 2\text{e}^- = \text{H}_2$	equilibrium
$\text{Fe}(\text{OH})_3 \leftrightarrow \text{Fe}^{3+} + 3\text{OH}^-$	equilibrium
$\text{Fe}^{3+} + 0.5\text{H}_2 \leftrightarrow \text{Fe}^{2+} + \text{H}^+$	-53.44
$\text{SO}_4^{2-} + \text{H}^+ + 4 \text{H}_2 \leftrightarrow \text{HS}^- + 4\text{H}_2\text{O}$	-9.64
$\text{HCO}_3^- + \text{H}^+ + 4\text{H}_2 \rightarrow \text{CH}_4 + 3\text{H}_2\text{O}$	-5.0
$\text{CH}_4 + 3\text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{H}^+ + 4\text{H}_2$	-5.0
$\text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$	equilibrium
$\text{FeS} + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{HS}^-$	equilibrium

It should be mentioned that sulfate reduction and Fe-oxide reduction are in principle also reversible processes, and since they are not defined in the model with what could be termed an “energy-gap” as the methanogenesis / methane oxidation reaction pair is, these reactions are allowed to run in reverse. To what extent this occurs in real world anaerobic aquifer systems is currently not known however it turns out that with the parameters used here the reverse reactions are absent. In principle they should be defined in a manner similar to methanogenesis / methane oxidation but considering the already lengthy model run times on the available system this has not been tried. The reaction rate for the organic matter added in the stagnant zones was adjusted so that methanogenesis is occurring in the stagnant zones, Fe-oxide reduction in the active flow parts and sulfate reduction in both places. The macroscopic rate derived from the change in Fe(2) in the pore water observed across the 4 mm model system, when the other processes have been removed, during the 9000 seconds that the breakthrough takes turn out to correspond to around 100 mM/yr of reduced sulfate. This is about 20 times higher than the highest rates measured by radiotracer measurements in the Rømø formation (Jakobsen and Postma, 1999) on a core scale in volumes of 100-200 ml of core.

2.2 Model results

Figure 2 shows the distribution of Fe²⁺, sulfate, methane and H₂ in the model after it has reached a quasi-steady state where the redox state does not change and the bromide added as a tracer has reached a minimum of 99% of the input concentration in the entire model

domain. This occurs after approximately 30000 seconds using the bulk rate of 100mM/yr. With lower rates of organic matter oxidation the system was totally dominated by Fe-oxide reduction. By making Fe-oxide reduction thermodynamically less favorable, this could be changed but still sulfate reduction would dominate also in the stagnant micropores.

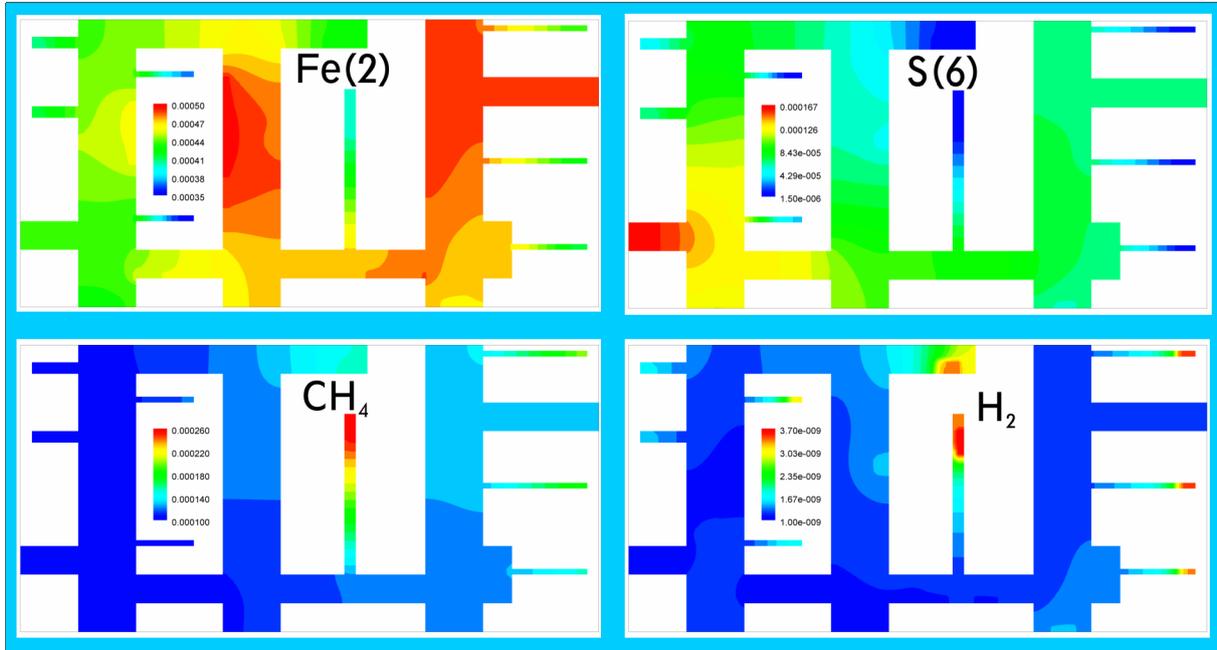


FIGURE 2. The distribution of Fe(2), sulfate methane and hydrogen in the pore water of the domain at a quasi-steady state, concentration in moles/kg of solution.

The model result indicates that it is possible to have methanogenesis occurring in the micro-niches of the dead-end pores concomitantly with Fe-oxide and sulfate reduction occurring in the system, but it is also clear from the model that these dead-end pores need to be relatively deep, even though the rate of organic matter oxidation is very high. In fact methane is only released from the most remote dead-end pores in the downstream more reduced part of the model. The methane produced is not all reoxidized because of the energy threshold for methane oxidation implemented in the model, so the actively moving water picks up methane as it passes the openings of the dead-end pores. The plots for Fe^{2+} and sulfate shows that Fe-oxide reduction occurs where the Fe-oxides are present, that sulfate is reduced in proximity to the organic matter and in the active channels and that there are sinks for Fe^{2+} as well as sulfide, indicating precipitation of FeS. This is also seen on Figure 3, where changes in the concentrations of Fe-oxide, Fe-sulfide and calcite during a 10 second time-step are shown. Comparing with Figure 1, we see that Fe-sulfides precipitate on the fringe of the Fe-oxide areas when these are hit by sulfide. It is also worth noting that the CO_2 released from the organic matter oxidation leads to a local sub-saturation for calcite, but due to the net use of acid by the Fe-oxide reduction, inspite of the precipitation of FeS, the calcite is reprecipitated on the Fe-oxide.

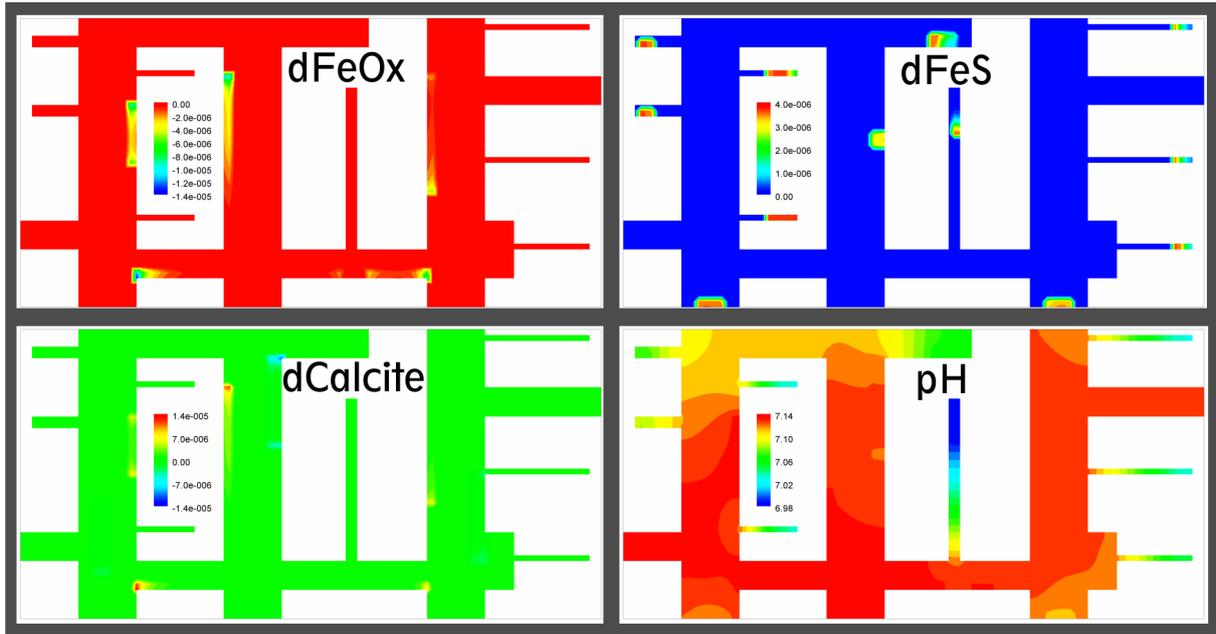


FIGURE 3. The amount (in moles pr. kg of solution) of equilibrium controlled solid phases reacting within a time step and pH in the model at a quasi-steady state, showing dissolution of Fe-oxide (negative values), precipitation of FeS (positive values) where organic matter is being added and dissolution and precipitation of calcite in response to pH changes induced by the redox reactions.

3. DISCUSSION

Though the model is only 2-D, rather than 3-D, and though a parabolic velocity distribution of the flow in the pores is not included in the model, it is the hope that the model leads to a, perhaps not quantitative, but still realistic picture of the type of geochemistry that could occur on the pore-scale in an aquifer system. The system modelled here, is comparable to the Rømø aquifer described by Jakobsen and Postma (1999). It is a young aquifer with relatively reactive organic material. Considering that methane is only produced in the deepest stagnant pores in this system, and only when the rate of organic matter oxidation seen macroscopically across the domain was 20 times higher than any value measured in the real system, it appears that a redox potential in the stagnant parts of intragranular scale, much lower than in the moving water, leading to localized methane production, is probably not so common in aquifers. Especially not in aquifers consisting of older sediments, where the organic matter is normally much less reactive. The diffusive transport appears to be too efficient compared to the rates of organic matter oxidation when the extent of the organic matter is small, This would imply that if stagnant zones are important they must be rather deep and narrow and the organic matter must be present in at least grain-sized lumps. The 1-D model of Jakobsen (2002) which could reproduce the observed geochemistry and had the correct overall rate of organic matter oxidation, is in a way also closer to a case where the organic matter is present as larger separate particles, since in that case the organic matter was

released in a specific fraction of the system, the 3%, of the pore volume entered as being stagnant.

4. CONCLUSIONS

The modelling indicates that grain-scale chemistry in an aquifer with a heterogeneous composition may be quite complex, both in terms of the inorganic and the organic geochemistry leading to the development of diverse redox regimes and the dissolution and precipitation of minerals in subdomains of the pore space. However, to have very large gradients in the redox potential, in the case of microbial redox processes, in e.g. the H₂ level requires rather reactive organic matter. The presence of low concentrations of methane in many aquifers, is more likely related to methane production occurring in lumps rich in organic matter and certainly if the aquifer is old and the organic matter low in reactivity.

REFERENCES

- Brun, A. and P. Engesgaard (2002), Modelling of transport and biogeochemical processes in pollution plumes: literature review and model development, *J. Hydrol.*, 256, 211-227.
- Curtis, G.P. (2003), Comparison of approaches for simulating reactive solute transport involving organic degradation reactions by multiple electron acceptors, *Comp. & Geosciences*, 29, 319-329.
- Hansen, L.K., R. Jakobsen, D. Postma (2001), Methanogenesis in a shallow sandy aquifer, Rømø, Denmark, *Geochim. Cosmochim. Acta*, 65, 2925-2935.
- Jakobsen, R. and D. Postma (1999), Redox zoning, rates of sulfate reduction and interactions with Fe-reduction and methanogenesis in a shallow sandy aquifer, Rømø, Denmark, *Geochim. Cosmochim. Acta*, 63, 137-151.
- Jakobsen, R. (2002), Including stagnant zones in order to model overlapping redox processes occurring in a shallow sandy aquifer, *Geochim. Cosmochim. Acta*, 66 (15A): A362-A362 Suppl. 1 AUG 2002
- Kipp, K.L., Jr. (1997), Guide to the revised heat and solute transport simulator: HST3D, *Water-Resources Investigations Report 97-4157*, 149 p, USGS, USA.
- Knutson, C.E., C.J. Werth and A.J. Valocchi (2005), Pore-scale simulation of biomass growth along the transverse mixing zone of a model two-dimensional porous medium, *Wat. Res. Res.*, 41(7): Art. No. W07007, 12p.
- Mayer, L.M. (1999), Extent of coverage of mineral surfaces by organic matter in marine sediments. *Geochim. Cosmochim. Acta*, 63, 207-215.
- Meile, C. and K. Tuncay (2006), Scale dependence of reaction rates in porous media. *Adv. Wat. Res.* 29 (1): 62-71.
- Parkhurst, D.L. and C.A.J. Appelo (1999), User's guide to PHREEQC (Version 2) *Water Resour. Inv. Rep.*, 99-4259. USGS, USA.
- Parkhurst, D.L., K.L. Kipp, P. Engesgaard, and S.C. Charlton (2005), PHAST—A Program for Simulating Ground-Water Flow, Solute Transport, and Multicomponent Geochemical Reactions, *U.S. Geological Survey Techniques and Methods 6–A8*, 154 p. USGS, USA.
- Postma, D. and R. Jakobsen (1996), Redox zonation: Equilibrium constraints on the Fe(III)/SO₄-reduction interface. *Geochim. Cosmochim. Acta*, 60, 3169-3175.
- Thullner, M., P. van Cappellen, P. Regnier (2005), Modeling the impact of microbial activity on redox dynamics in porous media, *Geochim. Cosmochim. Acta*, 69, 5005-5019.
- Watson, I.A., S.E. Oswald, S.A. Banwart, R.S. Crouch and S.F. Thornton (2005), Modeling the dynamics of fermentation and respiratory processes in a groundwater plume of phenolic contaminants interpreted from laboratory- to field-scale. *Environ. Sci. Technol.*, 39, 8829-8839.