

A Reactive Multi-Component Transport Model for Biodegradation of Petroleum Hydrocarbons

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Abstract A multi-component model accounting for hydrological transport, inorganic equilibrium chemistry and microbial activity during kinetically controlled biodegradation of compounds such as benzene, toluene, ethylbenzene and xylenes (BTEX) is presented. The problem is solved numerically using an operator-splitting method to couple advective-dispersive transport of organic and inorganic solutes with the geochemical equilibrium package PHREEQC and a biodegradation module. The transport equations for inorganic solutes are solved for total aqueous component concentrations. Changes in such concentrations due to precipitation/dissolution of minerals and chemical speciation are accounted for within PHREEQC. For chemical elements occurring in multiple valence states, separate components are defined and transported. The biodegradation module simulates the sequential or parallel activity of multiple bacterial groups attached to soils and their biochemical effects. An application of the model is shown for a case where BTEX compounds are degraded by sequential reduction of aqueous electron acceptors.

1. INTRODUCTION

In the last decade groundwater pollution by petroleum hydrocarbons has been reported extensively in the USA, Europe and Australia. The substantial costs involved in the remediation of such contaminated sites has led to increased interest in how these compounds degrade naturally (i.e., without intervention). As with active remediation schemes, where clean-up is achieved either by hydraulic measures or by stimulation of reactive processes, understanding of natural degradation processes requires a detailed understanding of the interactions between contaminants and the local biogeochemistry of a contaminated site. Modelling is aimed at quantifying the processes and their interdependencies.

Multicomponent reactive transport models that use the local equilibrium assumption (LEA) have been applied successfully to field-scale problems involving multiple reacting inorganic chemicals such as acidic mine tailings [Walter et al., 1994a,b]. However, reactions involving organic pollutants in most cases are not appropriately modelled by the LEA. Microbially mediated reactions such as the degradation of petroleum hydrocarbons typically are kinetically controlled rather than being in thermodynamic equilibrium, leading to a partial redox disequilibrium [McNab and Narasimhan, 1994]. Such a problem may be solved numerically by a fully kinetic formulation [Zysset et al., 1994] or, alternatively, by a mixed kinetic-equilibrium approach [Steeffel and MacQuarrie, 1996]. The latter approach has been used by, e.g., Brun et al. [1994] and McNab and Narasimhan [1994] to incorporate slow reaction kinetics into an equilibrium-based model. The solution procedure generally used is the operator-splitting method. This is seen as the only feasible method for solving realistic field-scale problems [Yeh and Tripathi, 1989]. It involves decoupling the physical transport and reactive processes. We have adopted this approach to simulate abiotic and biotic reactive processes during transport and biodegradation of BTEX and other petroleum hydrocarbon compounds.

2. MODEL DESCRIPTION

2.1 Advective-Dispersive Transport

In saturated porous media, the transport of a single reactive chemical is governed by:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} (D_{ij} \frac{\partial C}{\partial x_j}) - \frac{\partial}{\partial x_i} (\nu_i C) + R_c \quad (1)$$

where C is the aqueous concentration, ν_i is the pore velocity in direction x_i , D_{ij} is the hydrodynamic dispersion coefficient tensor, and R_c is a source/sink term. In a problem involving multiple reacting chemicals, R_c is a highly nonlinear function of the concentrations of other chemicals. Depending on the model approach, C may represent different entities such as aqueous species concentrations or total aqueous component concentrations [Yeh and Tripathi, 1989]. The latter are defined as:

$$C_j = c_j + \sum_{i=1, n_s} Y_{ij}^s s_i \quad (2)$$

where c_j is the concentration of the component in dissolved form and the second term on the right side represents the concentration of component j in the complexed species i , n_s is the number of complexed species in dissolved form, Y_{ij}^s is the stoichiometric coefficient of the j^{th} aqueous component in the i^{th} complexed species and s_i is the concentration of the i^{th} complexed species. In our model formulation, C represents either a total aqueous component concentration C_j or a concentration of an organic complex. Physical transport is carried out for:

$$n_{tot} = n_{e,nre} + \sum_{1, n_{rs}} n_{e,re} + n_{org} \quad (3)$$

different entities, where $n_{e,nre}$ is the number of chemical elements occurring in only one redox-state, $n_{e,re}$ is the number of elements occurring in multiple redox-states, n_{rs} is the

appropriate number of redox-states and n_{org} is the number of organic compounds. By carrying out physical transport separately for elements occurring in different redox states, we conserve the oxidation state during transport.

For organic compounds, the source/sink term R_c in (1) is obtained from:

$$R_c = R_{deg} + R_{dis} \quad (4)$$

where R_{deg} stands for concentration changes due to the biodegradation of this compound and R_{dis} is the concentration change due to non-equilibrium mass transfer from a NAPL phase. For all inorganic elements, the source/sink term in (1) is:

$$R_c = R_{min,ir} \quad (5)$$

where $R_{min,ir}$ equals the concentration changes obtained in the reaction step.

2.2 Equilibrium Reaction Module

For reactive transport governed by the LEA, a time-discretised form of the transport equation (1) for time-centred weighting is [Walter et al., 1994a]:

$$C^{n+1} - C^n = (L(C_k)^{n+1/2})\Delta t + R_{min,ir}^{equil} \quad (6)$$

$L(C_k)$ is the spatial differential operator, C^n and C^{n+1} are total aqueous component concentration at the old and new time level, respectively. $R_{min,ir}^{equil}$ is the difference in concentrations from before and after the reaction step. We have chosen the USGS package PHREEQC [Parkhurst et al., 1995] as the module to quantify $R_{min,ir}^{equil}$. The package handles the whole range of complexation, acid-base, oxidation-reduction, precipitation-dissolution, gas-phase, ion-exchange and adsorption reactions.

We use PHREEQC to (i) carry out irreversible reactions to account for the mineralisation of organic compounds and the incorporation of inorganic species into biomass; (ii) simultaneously equilibrate the aqueous solution with respect to n_p minerals included in the simulation; and (iii) determine aqueous species concentrations (speciation). The quantities added in (i) are determined by the biodegradation module. They couple the non-equilibrium degradation reaction of the organic compounds with the LEA-based inorganic chemistry. Numerically, in the reaction step PHREEQC solves a set of algebraic equations by the Newton-Raphson method. The equations are derived from $n_{c,nre} + \sum_{1,n_{rs}} n_{e,re}$ mole-balance equations, $n_s + n_p$ mass-action equations, one charge-balance equation for the aqueous phase, one for the ionic strength of the solution and one for the activity of water. The charge-balance equation is used to calculate hydrogen concentration (pH), thus no transport simulation is carried out for pH . Furthermore there is no need to transport pE as we consider multivalent elements separately.

2.3 Biodegradation Module

During microbially mediated degradation, electrons are transferred from inorganic aqueous species such as O_2 , NO_3^- , SO_4^{2-} (electron acceptors) or from minerals such

as $Fe(OH)_3$ to organic compounds such as benzene or toluene. The geochemical changes within the aqueous and mineral phases caused by the complete mineralisation of an organic compound can be modelled with PHREEQC as an irreversible reaction. This is achieved by adding concentrations of, e.g., $C_{C_6H_6}$ for benzene, $C_{C_7H_8}$ for toluene, etc. to the aqueous solution/mineral assemblage. In the same way, if we assume a specific biomass composition (e.g., $C_5H_7O_2N$), it is possible to consider the effects of the incorporation of inorganic species into a biofilm/biophase or, vice versa, of decaying biomass. As we assume that the LEA does not hold for the degradation reaction of an organic compound, only $\Delta C_{org,deg}$ mineralises during a time interval Δt and the change of biomass concentration for this time interval is ΔX . The biodegradation module is used to quantify $\Delta C_{org,deg}$ for all organic compounds and ΔX for n_{mic} different microbial groups catalysing the degradation reaction. Therefore, we consider a system of multiple microbial populations attached to the aquifer matrix. We distinguish each bacterial group by the electron acceptor used. Optionally, a facultative use of electron acceptors may be defined, e.g., aerobes/denitrifiers may form one bacterial group. For the degradation of multiple organic compounds, the mass balance for the k^{th} microbial population is:

$$\frac{\partial X_k}{\partial t} = \sum_{n=1, n_{org}} \frac{\partial X_{k,n}}{\partial t} - v_{decX_k} X_k \quad (7)$$

where $\partial X_{k,n}/\partial t$ is the uptake rate by degradation of the n^{th} organic compound and v_{decX_k} is the decay rate for the k^{th} population. The rate of change of the k^{th} population during degradation of the n^{th} organic compound is assumed to be modelled by [Kindred and Celia, 1989]:

$$v_{sub}^n = v_{max}^n \lambda I_{nc} \left\{ \left(\frac{C_1}{K_1^n + C_1} \right) \left(\frac{C_{ea}}{K_{ea}^n + C_{ea}} \right) \dots \left(\frac{C_m}{K_m^n + C_m} \right) \right\} X_k^n \quad (8)$$

where $v_{k,n}^{max}$ is the maximum uptake of the k^{th} population during degradation of the n^{th} organic compound and λ ($0 < \lambda < 1$) is a factor accounting for diffusional transport of organic compounds, electron acceptors and nutrients into the immobile biofilm. C_n , C_{ea} and C_{nut} are the concentrations of the n^{th} organic compound, the electron acceptor used by the k^{th} population and any nutrient potentially limiting growth, respectively. I_{nc} ($0 < I_{nc} < 1$) is an inhibition factor which depends on the presence of inhibiting substances, K_n , K_{ea} and K_{nut} are half saturation constants for the n^{th} organic compound, the electron acceptor used by the k^{th} population and nutrients, respectively. To account for a potential diffusional limitation of microbial growth, the concept of an effectiveness factor

$$\lambda = \frac{\theta_{bio,max} - X_{tot}}{\theta_{bio,max}} \quad (9)$$

is included in (8), where $\theta_{bio,max}$ is a maximum capacity and X_{tot} , the total bacterial concentration of all n_{pop} populations is given by:

$$X_{tot} = \sum_{i=1, n_{pop}} X_i \quad (10)$$

For small biomass concentrations corresponding to a thin biofilm with little or no diffusional limitation of microbial activity, λ has no limiting effect, however, for a biomass concentration approaching the maximum capacity, λ approaches 0, as does microbial growth. Originally the concept was proposed for a single microbial population by Atkinson and Davies [1974] and applied more recently by Zysset et al. [1994].

The degradation of the organic compounds and microbial growth are linked via their stoichiometry, thus the source/sink R_{deg} for the n^{th} organic compound can be derived from:

$$R_{deg} = \frac{\partial C_{org,deg}}{\partial t} = \sum_{k=1, n_{pop}} Y_{k,n} \frac{\partial X_{k,n}}{\partial t} \quad (11)$$

2.4 Dissolution of Residual Organic Compounds

In a typical scenario of a contamination by petroleum hydrocarbons, e.g., via a leaking underground storage tank, free product such as gasoline migrates downwards through the unsaturated zone until it reaches the capillary zone. There, the mobility of the hydrocarbons decreases as water saturation increases and accumulation takes place above the water table. Water table fluctuations cause a vertical smearing of the free product, thus increasing the contact zone between free product and groundwater. In this zone dissolution of NAPL compounds acts as a continuous contamination source for the groundwater. For simplicity, the NAPL pool in our model is assumed to be immobile and mass losses other than by dissolution (e.g., by vaporisation), are neglected.

For the n_{org} organic compounds, non-equilibrium mass transfer R_{dis} from a NAPL pool may be expressed as:

$$\frac{\partial C_i^{diss}}{\partial t} = \omega_i (C_i - C_{sat,mc}^i) \quad (12)$$

where ω_i is a rate-transfer coefficient approaching infinity for equilibrium dissolution, C_i is the aqueous species concentration of the i^{th} organic compound and $C_{sat,mc}^i$ is the multi-component solubility of the i^{th} organic compound. The multi-component solubility is calculated according to Raoult's law:

$$C_{sat,mc}^i = C_{sat}^i \gamma_i m_i \quad (13)$$

where C_{sat}^i is the single-species solubility, γ_i is the activity coefficient of the i^{th} organic compound and m_i is the mole fraction of the i^{th} organic compound. The mole fraction is defined as:

$$m_i = \frac{n_i}{n_{tot}} \quad (14)$$

where n_i is the molar concentration of compound i in the NAPL phase and n_{tot} is the total molar concentration of all organic compounds in the NAPL phase.

2.5 Solution algorithm

A one-dimensional finite-difference transport simulator with central weighting in space and time was used to solve

physical transport as defined in (1). For coupling of the transport model with the other modules, two different solution schemes, a sequential and an iterative operator-splitting method, were implemented. Both algorithms are based on the ones proposed by Walter et al. [1994a] for pure equilibrium problems. Subsequently, we describe only the iterative mode, which is the more accurate solution. However, for problems in two and three spatial dimensions, the sequential solution becomes more attractive due to its significantly higher computational efficiency.

In the iterative mode, at a time level t^n an initial guess for R_c is made and the transport equation including the source/sink term R_c is solved, leading to estimates of aqueous concentrations for the next time level t^{n+1} . The iteration scheme improves these estimates. In the subsequent step, R_{deg} and R_{dis} are determined, using concentrations centrally weighted in time. In the case of aqueous component concentrations C^n and C^{n+1} are concentrations from before and after the transport step, respectively. For other concentrations at t^{n+1} , such as concentrations of residual NAPL or mineral concentration, estimated values are used in the first iteration, i.e., using:

$$C^{n+1} = C^n + \left(\frac{\Delta C}{\Delta t}\right)^{n-1} \quad (15)$$

Finally, $R_{min,ir}^{equil}$ is determined, also using time-centred concentrations. The concentrations (aqueous, mineral, microbial, NAPL) for t^{n+1} derived in the previous steps provide now improved estimates of C^{n+1} for the next iteration cycle. The iteration is carried out until for all aqueous components the source/sink terms R_c being used in the transport step are close to the source/sink term derived from the subsequent reaction steps.

3. MODEL EVALUATION

In general, verification of reactive transport models by comparison with analytical solutions is limited to a few simple cases. For more complex problems, the comparison of individual modules with independently developed models offers an important method of model testing. For our model, key issues are the correct coupling between transport and reaction and the appropriate simulation of the redox-state. We have tested our model for a one-dimensional redox problem presented by Walter et al. [1994a], involving the geochemical processes occurring when acidic mine tailings leach into an anaerobic carbonate aquifer. The LEA is made for all reactions. In the test problem, an acidic inflow solution leads to the formation of multiple dissolution/precipitation fronts with calcite being the first pH -buffering mineral to be removed completely, followed by siderite and finally gibbsite. The pE of the solution is completely controlled by the redox-couple $Fe(II)/Fe(III)$ with the $Fe(II)$ solubility being controlled by the pH . The simulation includes 14 aqueous components (12 of which are transported), 54 aqueous species and six minerals. The initial concentrations for the aqueous components and minerals as well as the inflow concentrations are shown in Table 1. Figure 1 shows a comparison between our model and the finite-element model MINTRAN [Walter et al., 1994a] for concentrations of selected components and minerals after 6, 12 and 24 days, derived from simulations in sequential

Table 1: Aqueous and mineral concentrations used in the mine tailing and the biodegradation simulations.

Aqueous component ¹	$C_{backgr.}$	C_{inflow}	$C_{backgr.},$ C_{inflow}
	Eval. case [moles/l]	Eval. case [moles/l]	BTEX case [moles/l]
pH	6.96	3.99	7.68
pE	1.67	7.69	12.85
O(0)	-	-	2.47E-04
N(5)	-	-	5.00E-04
N(3)	-	-	1.52E-16
N(0)	-	-	1.25E-15
N(-3)	-	-	0.0
C(4)	3.94E-03	4.92E-04	1.83E-03
S(6)	7.48E-03	5.00E-02	1.40E-03
S(-2)	-	-	0.0
Fe(2)	5.39E-05	3.06E-02	2.57E-24
Fe(3)	2.32E-08	1.99E-07	3.38E-14
Mn(2)	4.73E-05	9.83E-06	-
Ca	6.92E-03	1.08E-02	1.73E-03
Mg	1.96E-03	9.69E-04	1.03E-03
Na	1.30E-03	1.39E-03	7.25E-03
K	6.65E-05	7.93E-04	1.26E-04
Cl	1.03E-03	1.19E-04	7.81E-03
Al	1.27E-07	4.30E-03	-
Si	1.94E-03	2.08E-03	-
Mineral			
Calcite	1.95E-02	-	5.00E-03
Goethite	-	-	1.17E-02
Siderite	4.22E-03	-	0.0
Pyrite	-	-	0.0
Gibbsite	2.51E-03	-	-
Fe(OH)3(a)	1.86E-03	-	-
Gypsum	0.0	-	-
SiO2(a)	4.07E-01	-	-
NAPL			
Benzene	-	-	1.90E-01
Toluene	-	-	5.21E-01
Ethylbenz.	-	-	2.29E-01
Xylenes	-	-	4.54E-01
Propylb.	-	-	7.80E-02
Trim.pent.	-	-	1.34E+01

¹Values in parentheses indicate valence

operator-splitting mode. The models compare very well. The remaining differences are most likely due to small differences in the databases of the geochemical equilibrium models used.

4. SIMULATION EXAMPLE

A one-dimensional simulation was carried out to illustrate all the processes simulated in the model. The scenario chosen demonstrates how the degradation of organic contaminants changes successively the inorganic geochemistry of an originally uncontaminated aquifer system. We assume an idealised aquifer of length $l = 80$ m, being contaminated with residual NAPL between $x = 5$ m and $x = 9$ m from the influent end. Benzene, toluene, ethylbenzene, xylenes, propylbenzene and trimethylpentane are assumed to be the constituents of the NAPL mixture, defining the contamination source. The initial groundwater is assumed to be

aerobic and sulphate-rich and to be in equilibrium with respect to calcite and goethite. The influent concentration at $x = 0$ is the same as the initial groundwater composition. The aqueous component, minerals and NAPL's included in the simulation and their concentrations are shown in Table 1, the transport parameters are shown in Table 2. Figure 2 shows concentration profiles of selected organic and inorganic compounds at three different times ($t = 18, 80$ and 240 days) after the start of the simulation. Initially ($t = 0$), no dissolved organic compounds are present in the aquifer. As groundwater passes the contaminated zone, the constituents of the NAPL phase are dissolved. For the mass transfer coefficient and pore velocity chosen in this simulation, the dissolution becomes rate-limited as indicated in Figure 2 by steadily increasing concentrations within the fringes of the contamination source. The concentrations of dissolved benzene and toluene become significantly higher than concentrations of other organic compounds.

Table 2: Transport parameters used in the mine tailing and the biodegradation simulations.

Transp. parameter	Eval. case	BTEX case
Grid spacing [m]	0.05	1.0
Model length [m]	0.40	80.0
Pore velocity [m/d]	0.02	0.25
Porosity	0.35	0.30
Disp. coef. [m ² /d]	0.0001	0.20
Grid Péclet number	1.0	1.25
Courant number	0.5	0.125

The presence of organic substrates and oxygen as the most energetically favourable electron acceptor allows rapid growth of facultative aerobic/denitrifying bacteria near the contamination source (see Figure 2, $t = 18$ days). In the zone of aerobic degradation, calcite dissolves and buffers the pH which is thus hardly changed. After 8 days, oxygen is depleted near the contamination source, resulting in a switch to the reduction of N(5). As we assume that facultative degraders can use a secondary electron acceptor without any lag-period, N(5) is depleted soon after oxygen near the source. In this zone, the concentration of sulphate-reducing bacteria increases, as their growth is no longer inhibited by the presence of O(2) and N(5). The depletion of N(5) is accompanied by a massive drop in the pE of the solution. The plots in Figure 2 for $t = 18$ days show the beginning of this transition stage from denitrifying to predominantly sulphate-reducing activity at the contamination source. The sulphate reduction is accompanied by sulphide production. However, the presence of goethite in the mineral assemblage leads to a nonenzymatic formation of pyrite, being a sink for the sulphides in the aqueous solution.

The plots in Figure 2 for $t = 80$ days show that the sulphate-reducing zone is confined between the contamination source and the moving front of the contamination plume, where aerobic and N(5)-reducing degradation still prevails. The pH in the sulphate-reducing zone is again buffered by the carbonate system. However, here the aqueous solution gets oversaturated with respect to calcite which precipitates after equilibration, as can be seen in Figure 2.

At around $t = 240$ days, the non-degraded fraction of organic compounds reaches the model boundary. The profiles of aqueous components and of the microbial concentrations

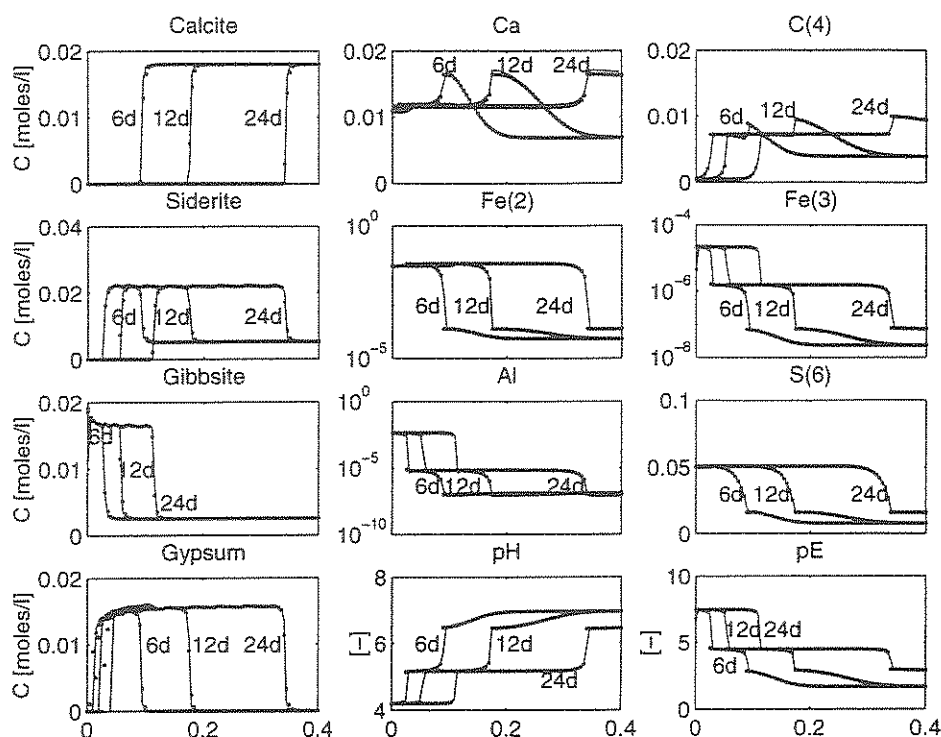


Figure 1: Selected aqueous component and mineral concentrations for our model (solid lines) and MINTRAN (...) at $t = 6, 12$ and 24 days.

evolve towards a quasi steady state and change only slowly which, in our simulation, shows a considerable mineralisation of toluene, a complete mineralisation of ethylbenzene and xylenes, and a slow degradation of benzene within the anaerobic zone of the model aquifer.

5. CONCLUSIONS

A framework for the simulation of the physical and biochemical processes occurring in an aquifer contaminated with petroleum hydrocarbons is presented. An application to an illustrative one-dimensional contamination scenario demonstrates the model's ability to handle these complex interactions. A complete mole-balance for all chemical elements is achieved as all elements are distributed within either aqueous, gas, mineral or biophase.

The numerical solution of the model is based on an operator-splitting technique allowing a flexible, modular structure. Thus, it is possible to integrate easily an existing computational tool to solve the geochemical equilibrium part and provide an opportunity to cope with realistic three-dimensional field-problems by only replacing the transport model used in this study.

6. ACKNOWLEDGEMENT

We would like to thank J. Molson and D. W. Blowes from the Waterloo Centre for Groundwater Research for providing their data sets for the MINTRAN modelling results of the mine tailings problem.

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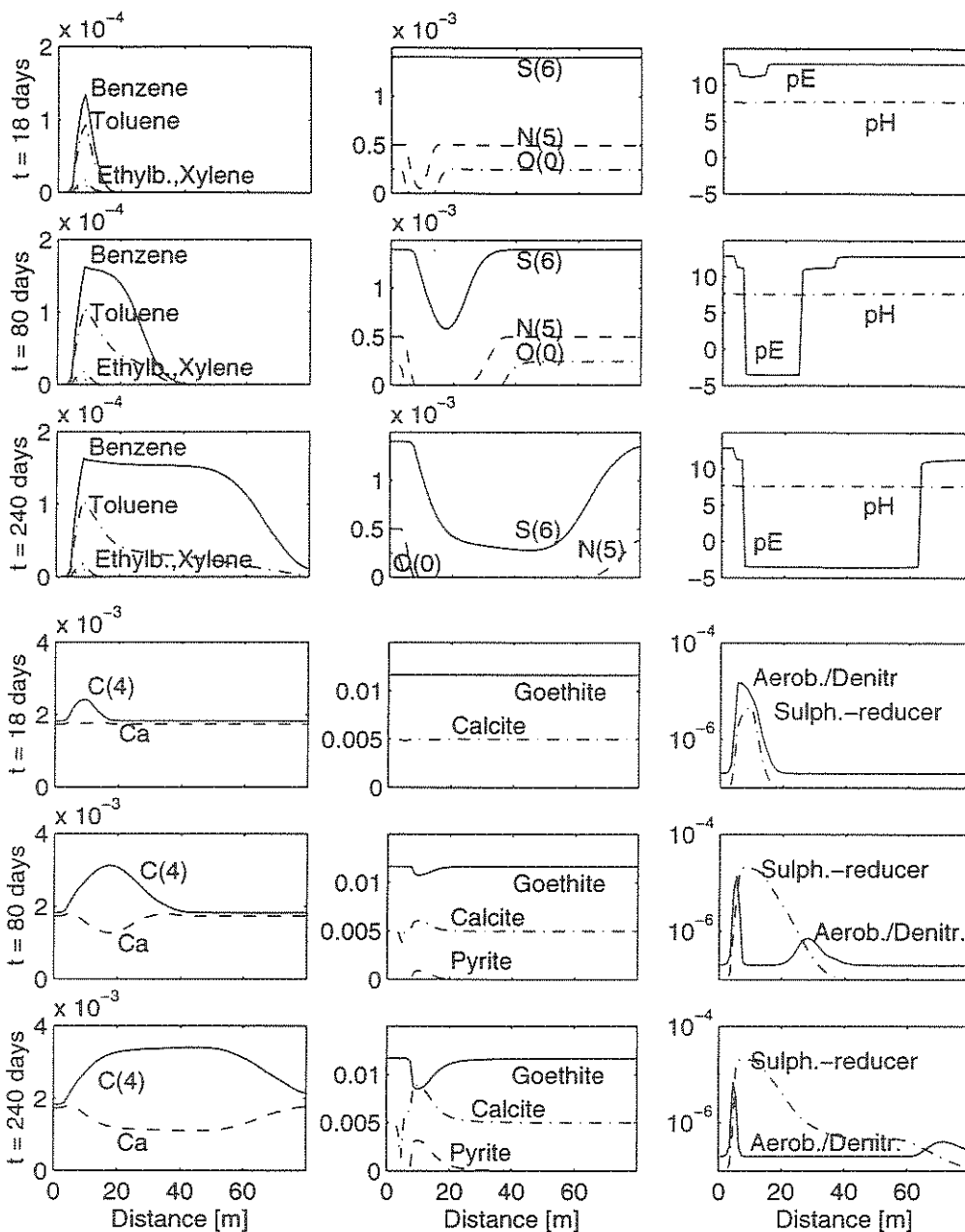


Figure 2: Selected aqueous component, mineral and bacterial concentrations at $t = 18, 80$ and 240 days. All concentrations are given as moles/l. Bacterial concentrations are moles $C_5H_7O_2N/l$.

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