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MODFLOW/MT3DMS-Based Reactive Multicomponent Transport Modeling

by H. Prommer^{1,2,3}, D.A. Barry⁴, and C. Zheng⁵

Abstract/

This paper presents a three-dimensional, MODFLOW/MT3DMS-based reactive multicomponent transport model for saturated porous media. Based on a split-operator technique, the model, referred to as PHT3D, couples the transport simulator MT3DMS and the geochemical modeling code PHREEQC-2. Through the flexible, generic nature of PHREEQC-2, PHT3D can handle a broad range of equilibrium and kinetically controlled reactive processes, including aqueous complexation, mineral precipitation/dissolution, and ion exchange. The diversity of potential applications is demonstrated through simulation of five existing literature benchmarks and a new three-dimensional sample problem. The model might be applied to simulate the geochemical evolution of pristine and contaminated aquifers as well as their cleanup. The latter problem class includes the natural and enhanced attenuation/remediation schemes of a wide range of organic and inorganic contaminants. Processes/reactions not included in the standard PHREEQC-2 database but typical for this type of application (e.g., NAPL dissolution, microbial growth/decay) can be defined and included via the extensible PHREEQC-2 database file.

Introduction

The more recent extension of the original single-species transport code MT3D (Zheng 1990) to the multi-species transport simulator MT3DMS (Zheng and Wang 1999) provided the starting point for the development of a number of models that simulate coupled hydrological transport of multiple chemical species and the chemical reactions among these species. For example, RT3D (Clement 1997) couples the implicit ordinary differential equation (ODE) solver LSODA to solve arbitrary kinetic reaction problems. RT3D provides a number of predefined reaction packages, e.g., for biodegradation of oxidizable contaminants consuming one or more electron acceptors and for

sequential decay chain-type reactions of chlorinated hydrocarbons (CHCs). The BIOREDOX model (Carey et al. 1999), SEAM3D (Waddill and Widdowson 1998) and MT3D99 (SSPA 1999) also simulate the fate of specific pollutants, i.e., BTEX and CHCs by solving purely kinetic biodegradation reactions. On the other hand, Guerin and Zheng (1998) presented GMT3D, a multicomponent transport model that addresses a whole range of reactive processes such as aqueous complexation and mineral dissolution/precipitation reactions by coupling the geochemical package HARPHRQ (Brown et al. 1991) to MT3DMS. While the aforementioned so-called "multispecies" models solve the transport equation separately for each aqueous complex, GMT3D and other "multicomponent" models solve for total aqueous component concentrations (Yeh and Tripathi 1989; Steefel and MacQuarrie 1996). However, in GMT3D and comparable models such as MINTRAN (Walter et al. 1994), all of the reactions included are treated as equilibrium reactions. This limits the applicability of the model to ground water systems where all reactions (of those chemicals included in a particular simulation) proceed relatively fast compared to the ground water flow, i.e., the local equilibrium assumption (LEA) is valid. Cases where the LEA often does not hold include the biodegradation reactions of many common organic substances and, for example, mineral weathering reactions. To (partially) overcome these limitations, Prommer et al. (1998, 1999a, 1999b) incorporated reaction modules for specific kineti-

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cally controlled processes (biodegradation, NAPL dissolution) into a model coupling MT3DMS and the (earlier) equilibrium-based PHREEQC model (Parkhurst 1995).

This paper presents the current version of the reactive multicomponent transport model PHT3D. It can handle general mixed equilibrium/kinetic geochemical reactions. Although other models with comparable features exist (Meyer 1999; Parkhurst et al. 1995; Schäfer et al. 1998; Steefel and Yabusaki 1996; Yeh et al. 1998), PHT3D combines the advantages of the well-established, modular and robust MODFLOW/MT3DMS flow/transport simulator family with the versatile capabilities and the reliability of the PHREEQC-2 (Parkhurst and Appelo 1999) model. Thus, a great variety of reactive transport problems can now be addressed for complex hydraulic systems and boundary conditions. Primarily, PHT3D model applications will target rather complex geochemical problems, i.e., multicomponent problems where transport and reactions of all major ions are included and pH, pe and, typically, water-rock (or water-sediment) interactions are simulated. Because the reaction part of the model is based on PHREEQC-2, reaction kinetics can easily be formulated through user-defined rate expressions within the database. Reactive processes such as NAPL dissolution and microbial growth/decay can thus conveniently be included through modifications of the original, extensible PHREEQC-2 database.

Model Description

The current version of the PHT3D model (version 1.0) couples the three-dimensional transport simulator MT3DMS (version 4.0) with the geochemical model PHREEQC-2 (version 2.5) through a sequential operator-splitting technique (Herzer and Kinzelbach 1989; Yeh and Tripathi 1989; Steefel and MacQuarrie 1996; Barry et al. 1996a, 1996b, 1997, 2002). Both models are widely used in the ground water/geochemistry communities and are individually well tested and documented. Thus, the subsequent sections describe the more specific aspects of combining both models into a comprehensive, multidimensional reactive transport simulator.

Hydrological Transport

The governing equation for both hydrological transport and reactions of the *i*th (mobile) aqueous species/component is (in indicial notation)

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x_\alpha} \left(D_{\alpha\beta} \frac{\partial C_i}{\partial x_\beta} \right) - \frac{\partial}{\partial x_\alpha} (v_\alpha C_i) + r_{\text{reac},i} \quad (1)$$

while for immobile entities, e.g., minerals, the transport terms drop out:

$$\frac{\partial C_i}{\partial t} = r_{\text{reac},i} \quad (2)$$

where v_α is the pore-water velocity in direction x_α , $D_{\alpha\beta}$ is

the hydrodynamic dispersion coefficient tensor, and $r_{\text{reac},i}$ is a source/sink rate due to chemical reaction. C_i is the total aqueous component concentration (Yeh and Tripathi 1989; Engesgaard and Kipp 1992), defined as

$$C_i = c_i + \sum_{j=1, n_s} Y_j^s s_j \quad (3)$$

where c_i is the molar concentration of the (uncomplexed) aqueous component, n_s is the number of species in dissolved form that have complexed with the aqueous component, Y_j^s is the stoichiometric coefficient of the aqueous component in the *j*th complexed species, and s_j is the molar concentration of the *j*th complexed species. The (local) redox-state, pe, is modeled by transporting chemicals/components in different redox states separately, whereas the pH is modeled from the (local) charge balance. The advection and dispersion terms within Equation 1, but not the reaction term, are solved by the transport module MT3DMS for each time step of a temporally discretised problem for n_{tot} entities, with

$$n_{\text{tot}} = n_{\text{e,nre}} + \sum_{k=1, n_{\text{e,ce}}} n_{\text{rs},k} \quad (4)$$

where $n_{\text{e,nre}}$ is the number of (mobile) chemical elements occurring in only one redox state, $n_{\text{e,ce}}$ is the number of elements occurring in multiple redox states, and $n_{\text{rs},i}$ is the appropriate number of different possible redox states of the *i*th element. Thus, if chemical elements might occur in multiple, i.e., $n_{\text{rs},i}$ different redox states within a simulation problem, an appropriate, higher number of separate transport equations has to be solved to predict correctly the redox state (pe). For example, transport of iron-complexes would typically require modeling the transport of Fe(II) and Fe(III) separately.

Geochemical Reactions

In PHT3D all concentration changes of aqueous components and immobile entities that result from reactive processes are computed by PHREEQC-2. It is, in contrast to its precursor models PHREEQE (Parkhurst et al. 1980) and PHREEQC (Parkhurst 1995), capable of simultaneously solving arbitrary, kinetically controlled reactions in addition to geochemical equilibrium problems. From the full set of geochemical reactions that can be handled by PHREEQC-2, a subset, including aqueous complexation, mineral precipitation/dissolution, and ion exchange has been implemented into the current version of PHT3D. This subset will be sufficient for most subsurface reaction/transport simulation problems. Note that, generally, the computation of the geochemical reaction step takes up most of the CPU-time required to solve coupled geochemical transport problems.

Coupling Procedure

Several options exist for the implementation of the split-operator method (e.g., sequential split-operator, alternating split-operator, iterative split-operator) to couple

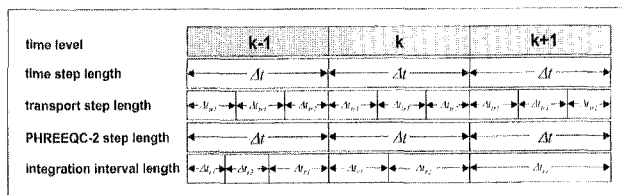


Figure 1. Time stepping scheme of the coupled transport and reaction model.

transport and reactive processes, and have been discussed in the literature (Yeh and Tripathi 1989; Zysset 1993; Zysset et al. 1994; Steefel and MacQuarrie 1996; Barry et al. 1996a, 1996b, 2002). The splitting technique applied in PHT3D is a modified version of the “standard” sequential split-operator technique.

Similar to the procedures previously applied to the case of the pure equilibrium reactive model (Walter et al. 1994) and the mixed equilibrium/kinetic model (Prommer et al. 1999b), the splitting technique used to solve the advection-dispersion-reaction Equation 1 for a user-defined time step length of Δt consists of two steps. In the first step, the advection and dispersion term of mobile entities is solved with MT3DMS for the time step length Δt . In the subsequent step, the reaction term r_{reac} in Equation 1 is solved through grid-cell wise batch-type PHREEQC-2 reaction calculations. This step accounts for the concentration changes that have occurred during Δt as a result of reactive processes. The reaction terms r_{reac} in Equations 1 and 2 correspond to the concentration differences from before (PHREEQC-2 input concentrations) and after the reaction step (PHREEQC-2 output concentrations). For aqueous components the initial concentrations for the PHREEQC-2 reaction simulations at the time level k (Figure 1) can be taken from the preceding transport step of the same time level, whereas for all immobile entities (such as minerals) the final concentrations from the previous reaction step at time level $k-1$ serve as initial concentrations.

In contrast to “standard” splitting schemes and depending on the actual advection scheme selected for a simulation, in PHT3D the user-defined time step length Δt might be further subdivided by MT3DMS into several transport steps of length Δt_{tr} (Figure 1) such that the relevant stability and/or accuracy criteria for physical transport (Courant number) is fulfilled. Thus, it is possible that several transport steps are carried out before a new reaction step occurs. If kinetic reactions are simulated, the PHREEQC-2 reaction step length will correspond to the (user-defined) time step length Δt , i.e., not to the automatically computed transport step length Δt_{tr} . Note that the latter varies depending on the actual advection scheme selected for the simulation. For the computation of kinetic reactions PHREEQC-2 uses a fifth order Runge-Kutta integration scheme (Fehlberg 1969). It divides the user-defined time step Δt into subintervals and, if a specified tolerance is not met for the error estimate of the integration, Δt will be integrated over two or more subintervals of length Δt_i (Figure 1), each of which is integrated with the fifth order scheme. Thus, the kinetic reactions are assured to be integrated accurately over the user-defined time interval Δt . Of

course, an increased (temporal) splitting error will still occur compared to a solution scheme or temporal discretization where transport and reaction steps alternate more often, e.g., at the frequency dictated by the transport step size. However, the model execution times (CPU-times) of the present scheme can be significantly lower, which often is helpful, particularly in the early, more conceptual stages of a modelling project, i.e., where (very high) solution accuracy is not a primary concern. Accuracy can be improved, of course, by reducing the size of Δt .

To reduce computational load, a further (optional) modification of the “standard” sequential split-operator technique was implemented in PHT3D. The modification allows the reaction step to be temporally omitted in cells where no reactive changes are expected. This modification exploits the fact that in many model applications there may exist zones, sometimes large, within the model domain where chemical gradients are negligible between neighboring grid-cells and where the aqueous solution is in equilibrium with the (local) mineral assemblage. In these zones, the reaction term r_{reac} computed by PHREEQC-2 might be zero for significant portions of the total simulation time and thus the reaction step, in principle, can be omitted during these periods. A typical case where this applies is a steadily spreading point source contamination within an initially, chemically homogeneous, equilibrated multidimensional model domain, where in the early stages of the simulation geochemical changes occur in a very small portion of the aquifer. This concerns in particular cases where advection is the dominant transport mechanism. To decide whether the reaction step in a particular grid-cell can be omitted, the joint fulfilment of the two criteria (three-dimensional case)

$$\sum_{k=\text{lay}-2l-\text{col}-2m=\text{row}}^{\text{lay}+2} \sum_{\text{col}+2}^{\text{col}+2} \sum_{\text{row}+2}^{\text{row}+2} \sum_{i=1}^{n_{\text{aq}}} \left| r_{\text{reac},k,l,m,i} \right| < \epsilon_{\text{aqu}}$$

$$(3 \leq k \leq \text{lay}_{\text{max}} - 2; 3 \leq l \leq \text{col}_{\text{max}} - 2; 3 \leq m \leq \text{row}_{\text{max}} - 2) \quad (5)$$

and

$$r_{\text{reac},\text{pH}} \quad (6)$$

has been found to be an efficient test, where $r_{\text{reac},k,l,m,i}$ is the computed reaction term for component i in layer k , column l and row m , both ϵ_{aqu} and ϵ_{pH} are user-defined accuracy criteria lay , col , and row are the actual indices of the layer, column and row of the (tested) grid-cell, respectively, and lay_{max} , col_{max} , and row_{max} are the total numbers of layers, columns, and rows, respectively in the model. The criteria (Equations 5 and 6) are tested for each grid-cell after a PHREEQC-2 reaction step. If both are fulfilled for a grid-cell, the execution of PHREEQC-2 (but not physical transport) is deactivated in this cell. Reactivation occurs automatically when either criterion (Equations 5 and 6) is not fulfilled, i.e., if reactive changes occur in neighboring grid cells. Grid-cells that receive external fluxes (e.g., through wells, rivers, recharge) cannot be deactivated and, furthermore, reaction simulations are always carried out for all grid-cells at the beginning of each new stress period, including the very first time step of the first stress period. Note that, for certain simulation problems, such as those

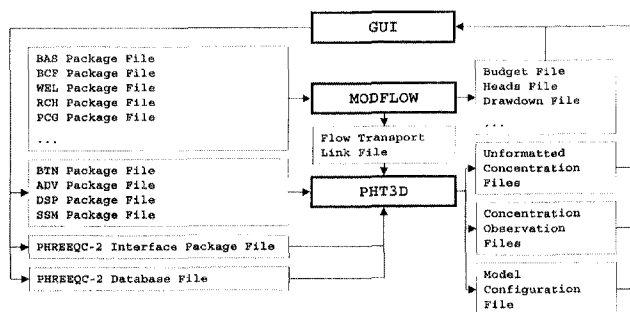


Figure 2. Data flow in a MODFLOW-based PHT3D simulation.

Table 1
Model Parameters of the Benchmark Example
by Parlange et al. (1984) and
Essaid and Bekins (1997)

Parameter	Value
Simulation time	1826 days
Time steps	200
Model length	150 m
Grid spacing (Δx)	1 m
Pore-water velocity	0.1 m/day
Dispersivity α_l	0 m
Inflow concentration C_0	1.0 mmol/L
Half saturation concentration K	0.5 mmol/L
Maximum uptake rate v_{\max}	4.77×10^{-3} /day

where the initial aqueous solution and/or the inflow solution across model boundaries are not in equilibrium with the mineral assemblage and mineral reactions are kinetically controlled, r_{reac} might always be nonzero in most or all grid-cells. A comparison of model execution times for the two cases with ($\epsilon_{\text{aqu}} = 1 \times 10^{-10}$ and $\epsilon_{\text{pH}} = 0.001$) and without omission of cells ($\epsilon_{\text{aqu}} = 0$ and $\epsilon_{\text{pH}} = 0$) is given in Table 9.

Model Structure

For the development of PHT3D, the original MT3DMS model has been used as a basis to incorporate an interface that prepares and executes the PHREEQC-2 reaction step. This model interface was kept relatively simple, which has the notable advantage that future, modified, and improved versions of not only the transport model but also the geochemical model can be quickly implemented with a modest effort. The model input/output for the existing MT3DMS features has not been changed. Compared to a "standard" MT3DMS simulation, only two additional input files are needed, one that contains information such as the names and types of chemicals, parameter values, and the stoichiometry of kinetic reactions and a second file that contains the definition of both equilibrium and kinetic reactions. The syntax of the latter file is analogous to that one used by the original PHREEQC-2 database file. Figure 2 shows the data flow within a typical PHT3D application.

Table 2
Model Parameters Used in the Benchmark Example
of Sun et al. (1999)

Parameter	Value
Simulation time	40 days
Time steps	40
Model length	40 m
Grid spacing (Δx)	1 m
Pore-water velocity v_x	0.4 m/day
Dispersivity α_l	10 m
First order rate constants, $k_A, k_B, k_{C1}, k_{C2}, k_{C3}$	0.2 d ⁻¹ , 0.1 d ⁻¹ , 0.02 d ⁻¹ , 0.02 d ⁻¹ , 0.02 d ⁻¹
Stoichiometric yield, $Y_B, Y_{C1}, Y_{C2}, Y_{C3}$	0.5, 0.3, 0.2, 0.1
Initial concentrations (all species)	0.0
Boundary inflow concentration C_0 for species A, B, C_1, C_2, C_3	1.0, 0.0, 0.0, 0.0, 0.0

Model Evaluation

To demonstrate the model capabilities and to verify the coupled model, a range of reactive multispecies and multi-component transport problems from the literature and published analytical solutions were used as benchmark problems for the evaluation of the individual reactive processes. Examples of these cases are briefly described here.

Single Species Transport with Monod Kinetics

In a first step, the numerical solution obtained by PHT3D was compared to the analytical solution for one-dimensional advective transport coupled to kinetically controlled biodegradation (Parlange et al. 1984; Essaid and Bekins 1997):

$$x = \frac{v}{v_{\max}} \left[K \ln \left(\frac{C}{C_0} \right) + C_0 - C \right] \quad (7)$$

with

$$\frac{\partial C}{\partial x} = 0 \quad \text{at } x = L \quad (8)$$

where x is a length coordinate in a one-dimensional domain of the total length L , C is the solute concentration, and C_0 is the concentration at the inflow boundary. Note that the solution (Equation 7) is based on a first-type boundary condition at the origin; Barry et al. (1993) provide the corresponding solution for a third-type boundary condition. Also, K is the half-saturation concentration, v_{\max} is the maximum uptake rate, and v is the pore-water velocity. All relevant model parameters and their values as used in the simulation are listed in Table 1. As can be seen in Figure 3, the numerical solution agrees very well with the analytical solution.

Multiple Species Transport with Kinetic, Sequential/Parallel Degradation

Sun et al. (1999) presented an analytical solution for one-dimensional advective-dispersive transport coupled to arbitrary multispecies series and/or parallel first-order reac-

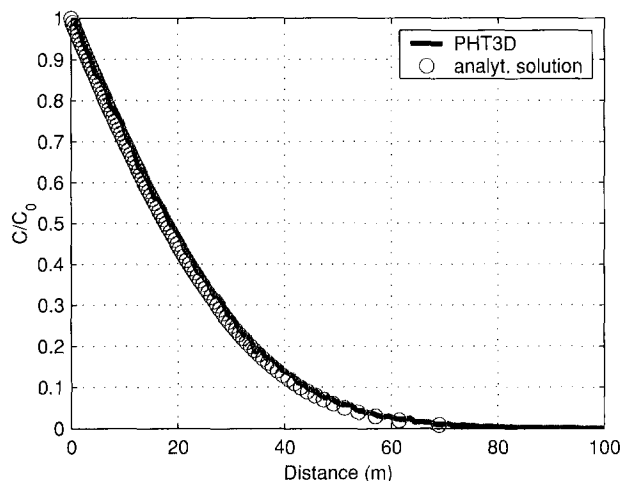


Figure 3. PHT3D simulation of single-species transport with Monod-type biodegradation in comparison with the analytical solution (Equation 7) of Parlange et al. (1984).

tions. In contrast to previously published analytical solutions for this type of problem, the solution is suitable for handling reactions with stoichiometric yields other than unity. Sun et al. (1999) applied their solution technique for a test case involving five degrading species and compared the results with a numerical solution computed with RT3D. The reaction network of their test case includes three possible reaction chains: $A \rightarrow B \rightarrow C_1$, $A \rightarrow B \rightarrow C_2$, and $A \rightarrow B \rightarrow C_3$. The governing equations for this reaction network are (Sun et al. 1999)

$$\frac{\partial C_A}{\partial t} - D \frac{\partial^2 C_A}{\partial x^2} + v \frac{\partial C_A}{\partial x} = k_A C_A \quad (9)$$

$$\frac{\partial C_B}{\partial t} - D \frac{\partial^2 C_B}{\partial x^2} + v \frac{\partial C_B}{\partial x} = y_B k_A C_A - k_B C_B \quad (10)$$

$$\frac{\partial C_{C1}}{\partial t} - D \frac{\partial^2 C_{C1}}{\partial x^2} + v \frac{\partial C_{C1}}{\partial x} = y_{C1} k_B C_B - k_{C1} C_{C1} \quad (11)$$

$$\frac{\partial C_{C2}}{\partial t} - D \frac{\partial^2 C_{C2}}{\partial x^2} + v \frac{\partial C_{C2}}{\partial x} = y_{C2} k_B C_B - k_{C2} C_{C2} \quad (12)$$

$$\frac{\partial C_{C3}}{\partial t} - D \frac{\partial^2 C_{C3}}{\partial x^2} + v \frac{\partial C_{C3}}{\partial x} = y_{C3} k_B C_B - k_{C3} C_{C3} \quad (13)$$

where C_A , C_B , C_{C1} , C_{C2} , and C_{C3} are the concentrations of the five species A, B, C_1 , C_2 , and C_3 , respectively, whereas y_A , y_B , y_{C1} , y_{C2} , and y_{C3} are stoichiometric coefficients and k_A , k_B , k_{C1} , k_{C2} , and k_{C3} are first-order reaction rate constants. All of the physical and chemical parameter values defining this benchmark problem are listed in Table 2. The PHT3D simulation results for this parameter set are shown in Figure 4 where they are compared with the analytical solution of Sun et al. (1999) and with additional numerical solutions computed with RT3D and PHREEQC-2 (using its ability to simulate one-dimensional advective-dispersive transport). All four solutions agree very well for all species except in proximity to the effluent end of the model domain.

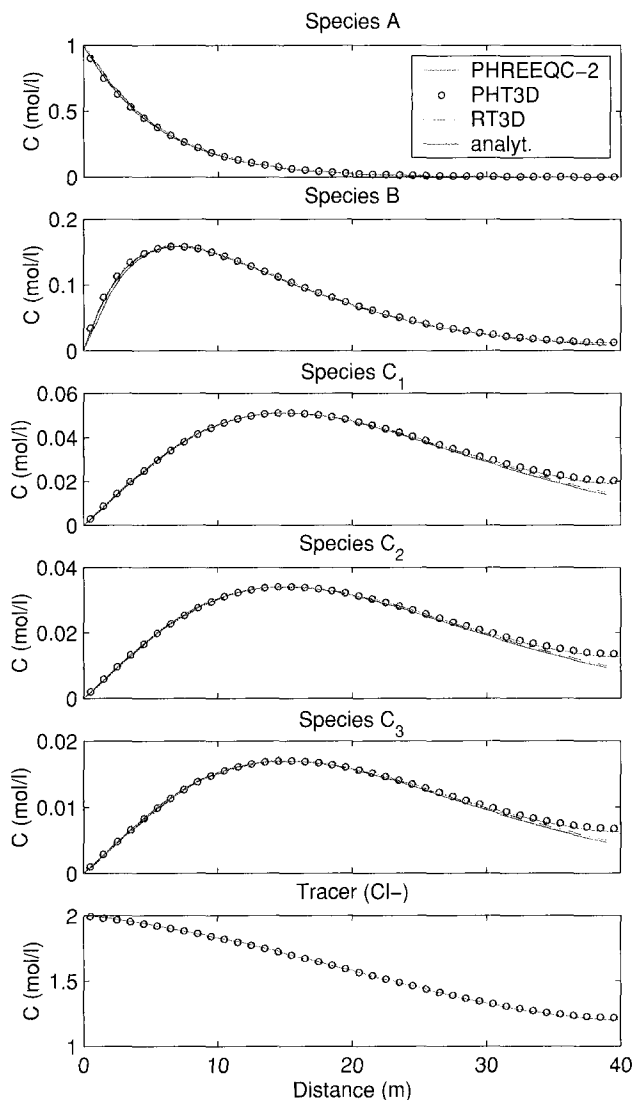


Figure 4. Comparison of simulated concentration profiles after 40 days for the modelling problem from Sun et al. (1999).

There, the RT3D model best matches the analytical solution whereas the PHT3D and PHREEQC-2 solutions exhibit some minor differences near the exit boundary.

Mineral Dissolution/Precipitation

The ability to quantify both equilibrium and kinetic-process-based mineral dissolution and precipitation reactions is important for the simulation of inorganic contamination problems such as acid mine drainage (AMD) and dissolved metal pollution. Moreover, it permits the study of such reactions occurring as primary (e.g., the reductive dissolution of $\text{Fe}(\text{OH})_3$) or secondary reactions (e.g., precipitation of FeS) during biodegradation of organic contaminants or of natural organic matter. Simulation problems presented by Engesgaard and Kipp (1992) and Walter et al. (1994) were used for verifying (equilibrium) mineral dissolution/precipitation reactions. The results of a model comparison between a PHT3D and a MST1D simulation (Engesgaard and Kipp 1992) are shown in Figure 5. The MST1D model is a precursor of the PHAST (Parkhurst et al. 1995) model and couples a one-dimensional version of

Table 3 Model Parameters Defining Hydrological Transport in the Benchmark Example by Engesgaard and Kipp (1992)	
Parameter	Value
Simulation time	0.2430 day
Time steps	210
Model length	0.5 m
Grid spacing (Δx)	0.005 m
Porosity	0.32
Pore-water velocity	0.083 m/day
Dispersivity α_l	0.0067 m

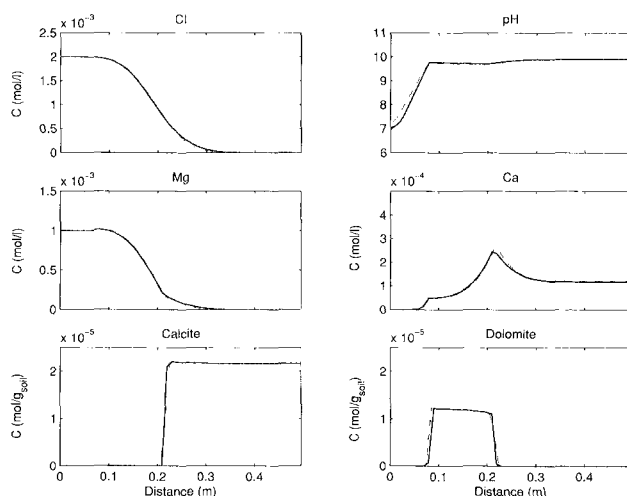


Figure 5. Comparison of simulated concentration profiles (after 21,000-s simulation time) between PHT3D (dotted lines) and MT1D (solid lines) for the mineral dissolution/precipitation test problem by Engesgaard and Kipp (1992). PHT3D results are plotted as dotted and MST1D results as solid lines.

HST3D (Kipp 1986) with PHREEQE (Parkhurst et al. 1980). In the simulation problem, an aqueous solution that is in equilibrium with the mineral calcite is flushed by a solution containing chloride and magnesium. As a result, a calcite dissolution front forms and migrates through the column. In the wake of the calcite dissolution front, dolomite precipitation and subsequent dissolution also occurs locally. The model comparison shows a very good agreement between the two models for the simulated aqueous and mineral concentrations, except for pH, where slight differences exist near the inflow boundary of the model domain. The relevant input parameters defining this problem are given in Tables 3 and 4.

Ion Exchange During Artificial Recharge

Simulation problems described by Starr and Parlange (1979), Appelo and Postma (1994), and Valocchi et al. (1981) served to evaluate the PHT3D model's capability of handling ion-exchange reactions. Only the case originally presented by Valocchi et al. (1981) is discussed here. It involves a field injection experiment where fresh water (pretreated municipal effluent) was injected into an alluvial brackish aquifer in the Palo Alto Baylands region. The

Table 4 Initial and Boundary Inflow Concentration Used in the Simulation of the Benchmark Example by Engesgaard And Kipp (1992)		
Component	Initial Concentration	Boundary Inflow Concentration
pH	9.91	N/A
pe	4*	N/A
C(IV)	1.23×10^{-4} mol/L	0.0 mol/L
Ca	1.23×10^{-4} mol/L	0.0 mol/L
Mg	0 mol/L	10^{-3} mol/L
Cl	0 mol/L	2×10^{-3} mol/L
Calcite	3.906×10^{-5} mol/L _{vol} ⁻¹ **	N/A
Dolomite	0 mol l _{vol} ⁻¹ **	N/A

*The simulation problem is not redox-sensitive.
**The initial mineral concentrations are given as mol/L bulk volume (not pore water).

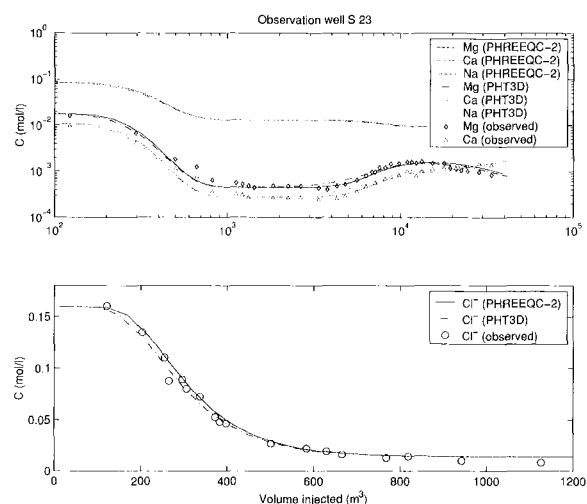


Figure 6. Comparison of simulated chloride and cation concentrations 16 m from the injection point for the modeling problem from Valocchi et al. (1981).

problem, which has been used previously as a benchmark problem by Zysset (1993), Barry and Bajracharya (1994), and Walter et al. (1994) involves nonreactive transport of chloride and the transport of three exchangeable heterovalent cations (Mg^{2+} , Ca^{2+} , Na^{+}) undergoing surface reactions. As described in more detail by Valocchi et al. (1981), the injection of the municipal effluent water at a rate of approximately 21 m³/hour created an essentially two-dimensional, radial flow field around the injection point. They simulated the resulting advective-dispersive transport using a modified one-dimensional model (Valocchi 1980) based on a solution provided by Rubin and James (1973). Zysset (1993) derived the relevant effective parameters of flow velocity and longitudinal dispersivity by fitting the analytical, one-dimensional model of van Genuchten (1980) to the observed breakthrough curve for chloride (Cl) at a borehole located 16 m from the injection point. Zysset (1993) found an average flow velocity of 27.0 m/day and a longitudinal dispersivity of 1.74 m. These values are in close agreement with those used by Barry and Bajracharya (1994). The breakthrough of the injected concentrations at

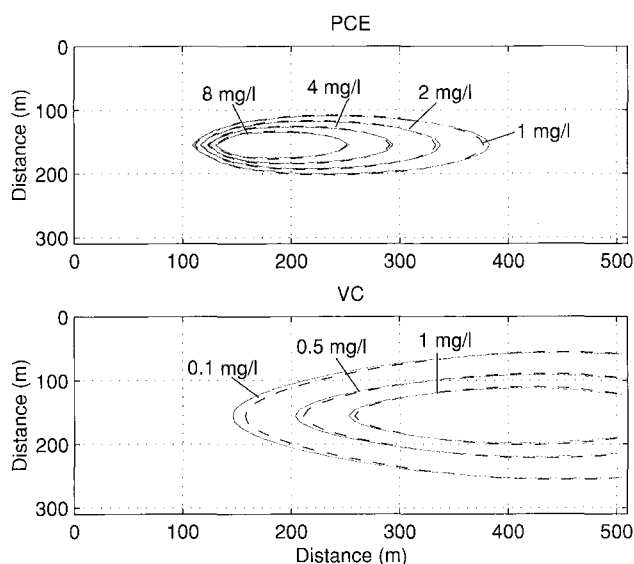


Figure 7. PHT3D simulation (—) of the sequential dehalogenation of PCE in comparison with the solution obtained by RT3D (---).

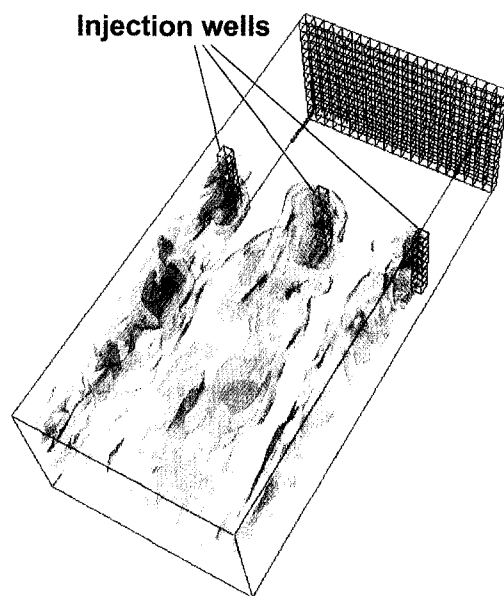


Figure 8. Nonreactive transport in the heterogeneous aquifer (concentration isosurfaces).

neighboring wells exhibits the chromatographic effects that result from the nonlinear ion-exchange processes. The parameters that define the transport problem are listed in Tables 5 and 6. In Figure 6, breakthrough curves simulated with PHT3D for chloride and for the cations are compared with results from a corresponding PHREEQC-2 simulation. In another test (results not shown), simultaneous dissolution/precipitation and ion-exchanging reactions were successfully verified using a problem presented by Sardin et al. (1986).

Biodegradation

Simulation of transport and reactions of chemicals that undergo biodegradation can be dealt with at different levels of process detail (Barry et al. 2002), starting with formula-

Table 5
Model Parameters Defining Hydrological Transport in the Benchmark Example by Valocchi et al. (1981)

Parameter	Value
Simulation time	83.33 days
Time steps	120
Model length	16 m
Grid spacing (Δx)	1 m
Porosity	0.35
Pore-water velocity	27.024 m/day
Dispersivity α_l	1.737 m

Table 6
Initial and Boundary Inflow Concentration Used in the Simulation of the Benchmark Example by Valocchi et al. (1981)

Component	Initial Concentration	Boundary Inflow Concentration
pH	7.286	N/A
pe	-1.555	N/A
C(IV)	2.588×10^{-3} mol/L	3.610×10^{-3} mol/L
Ca	1.120×10^{-1} mol/L	2.130×10^{-3} mol/L
Na	8.650×10^{-3} mol/L	1.466×10^{-3} mol/L
Mg	1.820×10^{-3} mol/L	9.400×10^{-3} mol/L
Cl	1.600×10^{-3} mol/L	5.000×10^{-3} mol/L
Ca-X ₂ *	1.526×10^{-1} mol/L	N/A
Na-X	1.593×10^{-1} mol/L	N/A
Mg-X ₂	1.427×10^{-1} mol/L	N/A

*X refers to the immobile, exchangeable concentration. The cation exchange capacity (CEC) in the simulations
The cation exchange capacity (CEC) is 0.75 mol/L.

tions where the reaction kinetics are independent of the concentrations of other chemicals, as shown in the single-species evaluation example. More complex formulations integrate the dependency of the reaction kinetics on the concentrations of other solutes (Clement 1997), explicitly model growth and decay of bacteria (Prommer et al. 2002), or even take into account the pH-dependency of bacterial growth (Brun and Engesgaard 2002). Two-dimensional simulation problems presented by Clement (1997) were used to verify kinetic multispecies biodegradation reactions (1) involving sequential first-order degradation of PCE and (2) for a Monod-type BTEX degradation that sequentially uses a predefined series of electron-acceptors (O_2 , NO_3^- , Fe^{3+} , SO_4^{2-} , CO_2). In both test cases, the organic contaminants were injected into a hypothetical homogeneous aquifer at a constant rate and at a constant concentration. A comparison of some PHT3D modeling results, i.e., PCE and VC (vinyl chloride) concentrations after three years with the solution obtained by RT3D, is shown in Figure 7 for the PCE example. The parameters that define this modelling problem are listed in Table 7. Despite the use of different solution techniques for the kinetic reactions, both solutions agree well.

Table 7
Model Parameters Defining Hydrological Transport in the Benchmark Example by Clement (1997)

Parameter	Value
Simulation time	1100 days
Time steps	55
Model extension	510 m × 310 m
Grid spacing ($\Delta x \times \Delta y$)	10 m × 10 m
Porosity	0.30
Hydraulic conductivity	50 m/day
Aquifer thickness	10 m
Head difference between inflow/outflow boundary	1 m
Dispersivity α_l	10 m
Well injection rate at contamination source	2 m ³ /day
PCE source concentration	6.031×10^{-3} mol/L
First order rate constants	$5.787 \times 10^{-8} \text{ d}^{-1}$, $3.472 \times 10^{-8} \text{ d}^{-1}$,
$k_{\text{PCE} \rightarrow \text{TCE}}$, $k_{\text{TCE} \rightarrow \text{DCE}}$, $k_{\text{DCE} \rightarrow \text{VC}}$, $k_{\text{VC} \rightarrow \text{ETH}}$	$2.314 \times 10^{-8} \text{ d}^{-1}$, $1.157 \times 10^{-8} \text{ d}^{-1}$

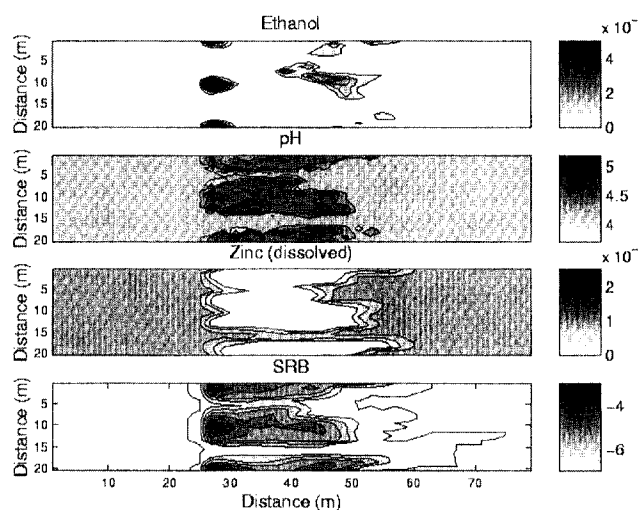


Figure 9. Concentration snapshot for a horizontal plane (Layer 6) of ethanol, pH, zinc, and SRB after 50 days simulation time. The concentration unit for ethanol, zinc, and SRB is mol/L (log-scale for SRB).

Sample 3D Application

A sample model application that combines typical reactive processes of inorganic pollution problems with the ones involved in biodegradation modeling is described here to demonstrate the potential of the PHT3D model. The case involves a hypothetical inorganic zinc contamination that is remediated by pulse-wise injection of a degradable organic substance. After an initial injection for 50 days, periods of natural ground water flow and injection alternate every 20 days, creating a transient flow field. During the degradation of the organic substance, a sulfate-reducing environment is created. The reducing zone acts as an in situ reactive zone that immobilizes dissolved metals, i.e., in the case presented here, through precipitation of sphalerite (ZnS). A hypothetical heterogeneous conductivity distribution cre-

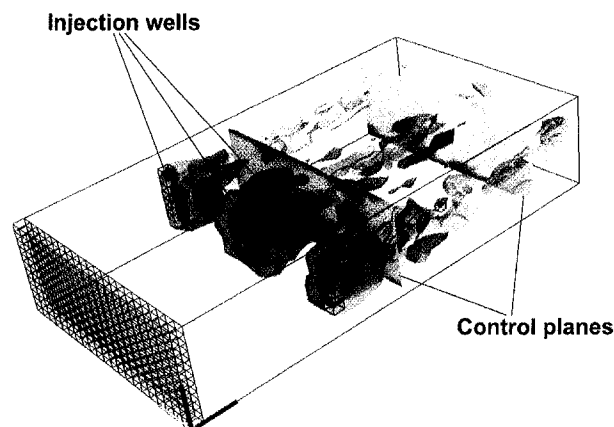


Figure 10. Aqueous zinc concentrations after 200 days in two control planes perpendicular to the main flow direction (red = initial aqueous zinc concentration, yellow = very low zinc concentration), and concentration isosurfaces of SRB (green) and ethanol (grey).

ates a nonparallel, three-dimensional flow field for the transport simulations. The model domain ($80 \text{ m} \times 21 \text{ m} \times 12 \text{ m}$) was discretized into equally sized grid cells ($2 \text{ m} \times 1 \text{ m} \times 1 \text{ m}$). The horizontal spacing of the injection wells (perpendicular to the flow direction) is 10 m. Due to symmetry, the injection rate of the outer two wells, located at the model boundaries, is 50% of the central well. The results (isoconcentration surfaces) from a nonreactive simulation in which a tracer was injected at a constant rate are shown in Figure 8. In the reactive transport simulations, acidic leachate, including zinc (see Table 8), enters the upstream model (inflow) boundary over the full depth of the aquifer while the injection wells have a filtered length of 7 m. The injected water has the same (anaerobic) chemical composition as the initial/inflow water but is enriched with an organic substance (ethanol, $\text{C}_2\text{H}_5\text{OH}$, 5 mmol/L). The presence of both sulfate and the degradable organic substance enable the growth of sulfate reducing bacteria (SRB) in the absence of more favorable electron acceptors. As a result of the microbial activity, sulfate is reduced to sulfide, which then complexes with zinc and precipitates. As a result of sulfate reduction, the pH of the ground water increases locally. Figure 9 shows the simulated concentrations of ethanol, pH, zinc, and SRB during an early stage of the remediation (50 days simulation time) for a horizontal plane (Layer 6). Figure 10 shows a three-dimensional visualization of selected aqueous component concentrations for a later time (after 200 days) at which quasi-steady-state conditions are established. It becomes clear that for a successful cleanup, i.e., the removal of zinc below a given target concentration, the (modeled) remediation scheme relies strongly on transverse dispersive mixing between the injected water and the ground water passing between the injection wells. With the numerical model, engineering design parameters such as well spacing, (water) injection rates, organic substance concentration, and the choice of organic substance, i.e., alternative chemicals can be studied and optimized.

Table 8
Chemical Composition of the Contaminated Ground Water (Initial and Boundary Inflow Concentrations)
in the Sample Application

Component	Concentration	Component	Concentration	Component	Concentration
S(VI)*	5.07×10^{-2} mol/L	Ca	1.10×10^{-2} mol/L	Mn(II)	9.98×10^{-6} mol/L
S(-II)	0.0	Mg	9.83×10^{-4} mol/L	Al	4.36×10^{-3} mol/L
Fe(II)	3.10×10^{-2} mol/L	Na	1.41×10^{-3} mol/L	Si	2.11×10^{-3} mol/L
Fe(III)	2.02×10^{-7} mol/L	K	8.05×10^{-4} mol/L	Zn	1.01×10^{-4} mol/L
C(IV)	4.92×10^{-4} mol/L	Cl	1.21×10^{-4} mol/L	pH	4.2

*Values in parentheses indicate valence state.

Table 9
Execution Times Required by PHT3D to Solve the Benchmark Problems and the 3d Sample Problem
on a Desktop PC

Case	Number of Grid-Cells	Number of Time Steps	Number of Chem. Entities ^Δ	CPU Time *(seconds)	
				$\epsilon_{\text{aqu}} = 1 \times 10^{-10}$ $\epsilon_{\text{pH}} = 0.001$	$\epsilon_{\text{aqu}} = 0$ $\epsilon_{\text{pH}} = 0$
Parlange et al. (1984)	150	200	3	58	66
Engesgaard and Kipp (1992)	50	210	8	5.6	23
Valocchi et al. (1981)	17	1000	11	35	53
Sun et al. (1999)	41	40	9	6.0	6.4
Clement et al. (1997)	1581	55	8	300	379
3D Sample Simulation	10080	260	18	24900	38820

[†]Operating System: Red Hat Linux 7.3, Processor: AMD Athlon XP 2000+, 1.67 Ghz
^ΔChemical entities, i.e., aqueous components, kinetic species, minerals and ion exchangers
*For the execution times in the left column, the reaction equations are not solved in cells where the ϵ_{aqu} and the ϵ_{pH} criteria are satisfied. For the execution times in the right column, the reaction equations are solved for all cells for all times.

Summary

This paper has presented a MODFLOW/MT3DMS-based reactive multicomponent transport model, its evaluation, and a sample application. It has been shown that the model is suitable for dealing with a wide variety of reactive transport problems on different levels of complexity and can accurately reproduce the solutions of benchmark problems from the literature. The execution times needed to solve those problems on a desktop PC are summarized in Table 9. Simpler multispecies model applications can be handled easily either through predefined reaction modules or through the creation/definition of new modules. As the coupled transport model is based on the two widely used (sub)models, MT3DMS and PHREEQC-2, more complex (bio)geochemical transport modelling applications are made accessible to many potential users. However, true multicomponent transport simulations will always require users to have a sound understanding of geochemical processes and concepts.

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References

- Appelo, C.A.J., and D. Postma. 1994. *Geochemistry, Groundwater and Pollution*. Example 10.13, Flushing of Na⁺ and K⁺ with a CaCl₂ solution. Rotterdam, Brookfield: A.A. BALKEMA.
- Barry, D.A., and K. Bajracharya. 1994. Application of an improved mixing cell model to equilibrium and nonequilibrium multispecies transport. In *Proceedings of the Sixth Biennial Conference on Computational Techniques and Applications: CTAC93*, ed. D. Stewart, H. Gardner, and D. Singleton, 103-111. Singapore: World Scientific.
- Barry, D.A., K. Bajracharya, and C.T. Miller. 1996a. Alternative split-operator approach for solving chemical reaction/groundwater transport models. *Advances in Water Resources* 19, 261-275.
- Barry, D.A., C.T. Miller, and P.J. Culligan-Hensley. 1996b. Temporal discretization errors in non-iterative split-operator approaches to solving chemical reaction/groundwater transport models. *Journal of Contaminant Hydrology* 22, 1-17.
- Barry, D.A., C.T. Miller, P.J. Culligan-Hensley, and K. Bajracharya. 1997. Analysis of split operator methods for nonlinear and multispecies groundwater chemical transport models. *Mathematics and Computers in Simulation* 43, 331-341.

- Barry, D.A., J.-Y. Parlange, and P.J. Hensley. 1993. Calculation of kinetic rate constants from steady-state soil profile concentration measurements. *International Journal for Numerical and Analytical Methods in Geomechanics* 17, 243-254.
- Barry, D.A., H. Prommer, C.T. Miller, P. Engesgaard, and C. Zheng. 2002. Modelling the fate of oxidizable organic contaminants in groundwater. *Advances in Water Resources* 25, 899-937.
- Brown, P.L., A. Haworth, S.M. Sharland, and C.J. Tweed. 1991. HARPHRQ: A geochemical speciation code based on PHREEQE. Harwell Lab. Report NSSR 188.
- Brun, A., and P. Engesgaard. 2002. Modelling of transport and biogeochemical processes in pollution plumes: Model formulation and development. *Journal of Hydrology* 256, 211-227.
- Carey, G.R., P.J. Van Geel, and J.R. Murphy. 1999. BioRedox-MT3DMS Version 2.0: A coupled biodegradation-redox model for simulating natural and enhanced bioremediation of organic pollutants—User's guide. Waterloo, Ontario, Canada: Conestoga-Rovers & Associates.
- Chiang, W.-H. 2001. 3D-Groundwater Explorer (GE)—A computer code for 3D visualization of groundwater models using PMWIN, MODFLOW, MT3DMS, PHT3D and RT3D. Bethesda, Maryland: S.S. Papadopoulos & Associates.
- Chiang, W.-H., and W. Kinzelbach. 2001. 3D-Groundwater modeling with PMWIN—A simulation system for modeling groundwater flow and pollution. Berlin: Springer-Verlag.
- Clement, T. P. 1997. A modular computer code for simulating reactive multispecies transport in 3-dimensional groundwater systems. Technical Report PNNL-SA-11720. Richland, Washington: Pacific Northwest National Laboratory.
- Engesgaard, P., and K.L. Kipp. 1992. A geochemical transport model for redox-controlled movement of mineral fronts in groundwater flow systems: A case of nitrate removal by oxidation of pyrite. *Water Resources Research* 28, 2829-2843.
- Essaid, H.I., and B.A. Bekins. 1997. BIOMOC: A multispecies solute-transport model with biodegradation. Technical Report 97-4022. U.S. Geological Survey Water-Resources Investigations Report.
- Fehlberg, E. 1969. Low-order classical Runge-Kutta formulas with stepsize control and their application to some heat transfer problems. Technical Report R-315. NASA.
- Guerin, M., and C. Zheng. 1998. GMT3D—Coupling multicomponent, three-dimensional transport with geochemistry. In *Proceedings of the MODFLOW'98 International Conference*, ed. E.P. Poeter, C. Zheng, and M.C. Hill. Golden, Colorado: Colorado School of Mines.
- Herzer, J., and W. Kinzelbach. 1989. Coupling of transport and chemical processes in numerical transport models. *Geoderma* 44, 115-127.
- Kipp, K.L., Jr. 1986. HST3D—A computer code for simulation of heat and solute transport in three-dimensional groundwater flow systems: Technical Report 86-4095. U.S. Geological Survey Water-Resources Investigations Report.
- Meyer, K.U. 1999. A numerical model for multicomponent transport in variably saturated porous media. Ph.D. thesis, Department of Earth Sciences, University of Waterloo.
- Parlange, J.-Y., J. L. Starr, D.A. Barry, and R.D. Braddock. 1984. Some approximate solutions of the transport equation with irreversible reactions. *Soil Science Society of America Journal* 137, 434-442.
- Parkhurst, D.L., D.C. Thorstenson, and L.N. Plummer. 1980. PHREEQE: A computer program for geochemical calculations: Technical Report 80-96. U.S. Geological Survey Water-Resources Investigations Report.
- Parkhurst, D.L. 1995. User's guide to PHREEQC: A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations. Technical Report 95-4227. U.S. Geological Survey Water-Resources Investigations Report.
- Parkhurst, D.L., P. Engesgaard, and K.L. Kipp. 1995. Coupling the geochemical model PHREEQC with a 3D multi-component solute transport model. In *Proceedings of the Fifth Annual V. M. Goldschmidt Conference*, Penn State University, University Park, Pennsylvania. St. Louis, Missouri: Geochemical Society.
- Parkhurst, D.L., and C.A.J. Appelo. 1999. User's guide to PHREEQC: A computer program for speciation, reaction-path, 1D-transport, and inverse geochemical calculations. U.S. Geological Survey Water-Resources Investigations Report 99-4259.
- Prommer, H., D.A. Barry, and G.B. Davis. 1998. The effect of seasonal variability on intrinsic biodegradation of a BTEX plume. In *Groundwater Quality: Remediation and Protection GQ '98*, ed. M. Herbert and K. Kovar, 213-220. IAHS-Publ. 250.
- Prommer, H., D.A. Barry, and G.B. Davis. 1999a. A one-dimensional reactive multi-component transport model for biodegradation of petroleum hydrocarbons in groundwater. *Environmental Modeling Software* 14, 213-223.
- Prommer, H., G.B. Davis, and D.A. Barry. 1999b. PHT3D: A three-dimensional biogeochemical transport model for modelling natural and enhanced remediation. In *Proceedings of Contaminated Site Remediation: Challenges Posed by Urban and Industrial Contaminants*, Fremantle, Western Australia; ed. C.D. Johnston, 351-358.
- Prommer, H., D.A. Barry, and G.B. Davis. 2002. Influence of transient groundwater flow on physical and reactive processes during biodegradation of a hydrocarbon plume. *Journal of Contaminant Hydrology* 59, 113-132.
- Rubin, J., and R.V. James. 1973. Dispersion-affected transport of reacting solutes in saturated porous media: Galerkin method applied to equilibrium-controlled exchange in unidirectional steady water flow. *Water Resources Research* 9, 1332-1352.
- Sardin, M., R. Krebs, and D. Schweich. 1986. Transient mass-transport in the presence of non-linear physico-chemical interaction laws: Progressive modelling and appropriate experimental procedures. *Geoderma* 38, 115-130.
- Schäfer, D., W. Schäfer, and W. Kinzelbach. 1998. Simulation of processes related to biodegradation of aquifers: 2. Structure of the 3D transport model. *Journal of Contaminant Hydrology* 31, 167-186.
- S.S. Papadopoulos & Associates Inc. (SSPA). 1999. MT3D99 Documentation and User's Guide. Bethesda, Maryland: SSPA.
- Starr, J.L., and J.-Y. Parlange. 1979. Dispersion in soil columns: The snow plow effect. *Soil Science Society of America Journal* 43, 448-450.
- Steeffel, C.I., and K.T.B. MacQuarrie. 1996. Approaches to modeling of reactive transport in porous media. In *Reactive Transport in Porous Media*, ed. P.C. Lichtner, C.I. Steefel, and E.H. Oelkers, 83-129.
- Steeffel, C.I., and S.B. Yabusaki. 1996. OS3D/GIMRT, software for multicomponent-multidimensional reactive transport: User manual and programmers guide. PNL-11166. Richland, Washington: Pacific Northwest National Laboratory.
- Sun, Y., J.N. Petersen, T.P. Clement, and R.S. Skeen. 1999. Development of analytical solutions for multispecies transport with serial and parallel reactions. *Water Resources Research* 35, 185-190.
- Valocchi, A.J. 1980. Transport of ion-exchanging solutes during groundwater recharge. Ph.D. diss., Department of Civil Engineering, Stanford University, Stanford, California.
- Valocchi, A.J., R.L. Street, and P.V. Roberts. 1981. Transport of ion-exchanging solutes in groundwater: Chromatographic theory and field simulation. *Water Resources Research* 17, 1517-1527.
- van Genuchten, M.Th. 1980. Determining transport parameters from solute displacement experiments, Version 1.0. Research Report No. 118, U.S. Salinity Laboratory, USDA, ARS, Riverside, California.

- Waddill, D.W., and M.A. Widdowson. 1998. SEAM3D: A numerical model for three-dimensional solute transport and sequential electron acceptor-based bioremediation in groundwater. Technical Report, Virginia Tech., Blacksburg, Virginia.
- Walter, A.L., E.O. Frind, D.W. Blowes, C.J. Ptacek, and J.W. Molson. 1994. Modeling of multicomponent reactive transport in groundwater: 1. Model development and evaluation. *Water Resources Research* 30, 3137-3148.
- Yeh, G.-T., K.M. Salvage, J.P. Gwo, J.M. Zachara, and J.E. Szecsody. 1998. HydroBioGeoChem: A coupled model of hydrologic transport and mixed biogeochemical kinetic/equilibrium reactions in saturated-unsaturated media. Report ORNL/TM-13668. Oak Ridge, Tennessee: Oak Ridge National Laboratory.
- Yeh, G.-T., and V.S. Tripathi. A critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components. *Water Resources Research* 25, 93-108.
- Zheng, C. 1990. MT3D, A modular three-dimensional transport model for simulation of advection, dispersion, and chemical reactions of contaminants in groundwater systems. Report to the Kerr Environmental Research Laboratory. Ada, Oklahoma: U.S. Environmental Protection Agency.
- Zheng, C., and P.P. Wang. 1999. MT3DMS: A modular three-dimensional multispecies model for simulation of advection, dispersion and chemical reactions of contaminants in groundwater systems: Documentation and user's guide. Contract Report SERDP-99-1. Vicksburg, Mississippi: U.S. Army Engineer Research and Development Center.
- Zysset, A. 1993. Modellierung des chemischen Zustandes in Grundwasser-Infiltrations-Systemen. Ph.D. diss., Institut f. Hydromechanik und Wasserwirtschaft, ETH Zürich, Switzerland.
- Zysset, A., F. Stauffer, and T. Dracos. 1994. Modeling chemically reactive groundwater transport. *Water Resources Research* 30, 2217-2228.