

PHT3D – A MODFLOW/MT3DMS-based reactive multi-component transport model

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ABSTRACT

PHT3D, a three-dimensional, MODFLOW/MT3DMS-based reactive multicomponent transport model is presented. The model couples, via an operator-splitting method, the transport simulator MT3DMS (Zheng and Wang, 1998) and the geochemical package PHREEQC-2 (Parkhurst and Appelo, 1999). Through the flexible, generic nature of PHREEQC-2, PHT3D can handle a broad range of equilibrium and kinetic reactive processes, including aqueous complexation, mineral precipitation/dissolution and ion exchange. The diversity of potential applications is demonstrated via simulation of literature benchmarks and new problems. The latter include applications involving natural and enhanced remediation of organic (e.g., BTEX, CHCs) and inorganic (e.g., metals) contaminants and the geochemical changes occurring during their degradation. Processes/reactions not included in the standard PHREEQC database but are typical for this type of application (e.g., NAPL dissolution, microbial growth/decay) can be defined and included via the PHREEQC database file. PHT3D has been integrated into the PMWIN pre/postprocessing package (Chiang and Kinzelbach, 2001). There, users can select from existing reaction packages/database-files or develop and integrate newly developed packages.

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, 1998) 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 pre-defined reaction packages, e.g., for biodegradation of oxidisable contaminants consuming one or multiple 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 (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 model that addresses a whole range of reactive processes such as aqueous complexation, mineral dissolution/precipitation and surface complexation reactions by coupling the geochemical package MODPHRQ (Brown et al., 1991) to MT3DMS. In contrast to the previous, so-called 'multi-species' models, the transport equation is not solved separately for each chemical species but for total aqueous component concentrations (Yeh and Tripathi, 1989). However, all reactions included are treated as equilibrium reactions, limiting the generality of the approach. Prommer et al. (1998, 1999a) incorporated reaction modules for specific kinetically controlled processes (biodegradation, NAPL dissolution) into a model coupling MT3DMS and the (earlier) equilibrium-based PHREEQC model (Parkhurst, 1995) to partially overcome these limitations.

This paper presents the latest version of the reactive multi-component transport model PHT3D that can handle general mixed equilibrium/kinetic geochemical reaction and thus addresses a much greater variety of reactive transport problems than other previously published MT3D/MTDMS-based models. Primarily, PHT3D model applications will target true geochemical problems, i.e., multi-component problems where transport and reactions of all major ions are included and pH, pe and, if needed, water-sediment interactions are simulated. Because the model is based on PHREEQC-2, however, reaction kinetics can easily be formulated through user-defined rate expressions within the database. Indeed, arbitrary (including simple) non-geochemical multi-species transport problems can also be addressed efficiently.

Typical environmental applications, e.g., NAPL dissolution and microbial growth/decay can conveniently be included (again, via the PHREEQC-2 database).

MODEL DESCRIPTION

The PHT3D model couples the three-dimensional transport simulator MT3DMS with the geochemical model PHREEQC-2. In contrast to its precursor models (Parkhurst et al., 1980, Parkhurst, 1995), PHREEQC-2 is, in addition to solving geochemical equilibrium problems, capable of solving kinetically controlled reactions, using a Runge-Kutta algorithm (Fehlberg, 1969). The reactive transport equation (solved by MT3DMS) for the (mobile) aqueous species/components is (in indicial notation):

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial C}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (v_i C) + r_{\text{reac}} \quad (1)$$

and for immobile entities, e.g., minerals:

$$\frac{\partial C}{\partial t} = r_{\text{reac}} \quad (2)$$

where v_i is the pore-water velocity in direction x_i , D_{ij} is the hydrodynamic dispersion coefficient tensor, r_{reac} is a source/sink rate due to chemical reaction and C is the total aqueous component concentration (Yeh and Tripathi 1989, Engesgaard and Kipp 1992), defined as:

$$C = c + \sum_{i=1, n_s} Y_i^s s_i \quad (3)$$

where c 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_i^s is the stoichiometric coefficient of the aqueous component in the i^{th} complexed species and s_i is the molar concentration of the i^{th} complexed species. The (local) redox-state, pH, is modeled by transporting chemicals/components in different redox states separately, while the pH is modelled from the (local) charge balance. Using a sequential operator-splitting technique (Herzer and Kinzelbach, 1989; Yeh and Tripathi, 1989; Steefel and MacQuarrie, 1996, Barry et al., 1996), the advection and dispersion terms within (1) are, for each time step of a temporally discretised problem, solved by the transport module MT3DMS for n_{tot} entities, with

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

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 and $n_{rs, i}$ is the appropriate number of different possible redox states of the i^{th} element. The reaction term r_{reac} in (1) is subsequently computed by PHREEQC-2. Similarly to the pure equilibrium reactive model presented by Walter et al. (1994) and the mixed equilibrium/kinetic model of Prommer et al. (1999b), the starting concentrations used in the reaction simulations are taken from after the transport step.

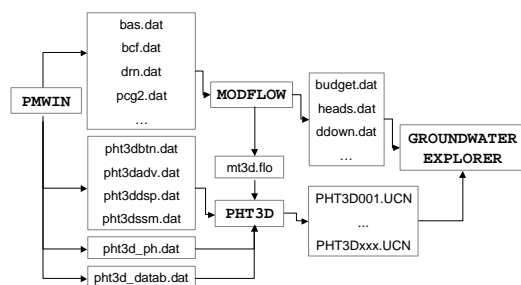


Figure 1. Data flow in a PHT3D simulation.

MODEL STRUCTURE

The original model structure of MT3DMS, in particular, of model input/output data-files has not been changed. However, compared to a "standard" MT3DMS simulation, two additional input files that (i) carry information about, e.g., the names and types of chemicals (pht3d_ph.dat) and (ii) a database file analogous to PHREEQC-2 database files (pht3d_datab.dat) are needed. In order to facilitate model I/O,

PHT3D was incorporated into PMWIN (Chiang and Kinzelbach, 2001). Fig.1 shows the data flow within a typical PHT3D application. Reactive species/components/minerals etc. and reaction parameters such as rate constants are managed by PMWIN, where reactive components may be added or removed from a simulation. Computed results, i.e., concentration values are visualized by PMWIN, the 3D visualization software Groundwater Explorer (Chiang, 2001) or packages such as MATLAB.

MODEL EVALUATION

In order to demonstrate the model capabilities and to verify the coupled model, a range of reactive multi-species 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. Some of these cases are briefly described here. Additional information is available from <http://www.pht3d.org> and full documentation can be found in Prommer et al. (2001b).

Single Species Transport with Monod Kinetics

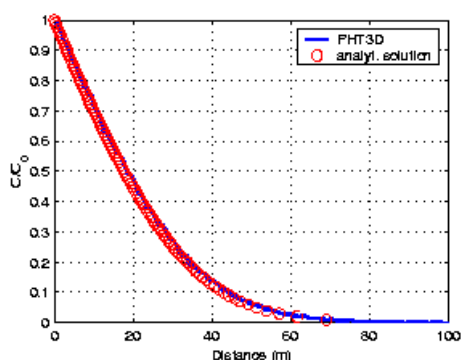


Figure 2. PHT3D simulation of single-species transport with Monod-type biodegradation in comparison with the analytical solution of Parlange et al. (1984)

10^{-3} d^{-1}) and the pore-water velocity (0.1 m d^{-1}). As can be seen in Fig. 2, the numerical solution shows some minor oscillations as a result of using the HMOC particle tracking scheme for solving advective transport but clearly agrees very well with the analytical solution.

Mineral Dissolution/Precipitation

The ability to quantify both equilibrium and kinetic process-based mineral dissolution and precipitation reactions is most important for the simulation of inorganic contamination problems such as acid mine drainage (AMD) and metal contamination. 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. A model comparison with the latter case was already presented in Prommer et al. (1999a) and is not repeated here.

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 model's capability of handling ion-exchange reactions. The latter case describes a field injection experiment where freshwater (pre-treated municipal effluent) was injected into an alluvial brackish aquifer in the Palo Alto Baylands region. The problem, which has been used previously as benchmark problem, e.g., by Walter et al. (1994) and Zysset (1993) involves non-reactive

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):

$$x = \frac{v}{v_{\max}} \left[K \ln\left(\frac{C}{C_0}\right) + C_0 - C \right], \quad (5)$$

with

$$\frac{\partial C}{\partial x} = 0 \quad \text{at } x = L, \quad (6)$$

where x is a length coordinate in a one-dimensional domain of the total length L , C is the solute concentration and C_0 (1 mg l^{-1} in the example) is the concentration at the inflow boundary. K , v_{\max} and v are the half-saturation concentration (0.5 mg l^{-1}), the maximum uptake rate ($4.77 \times$

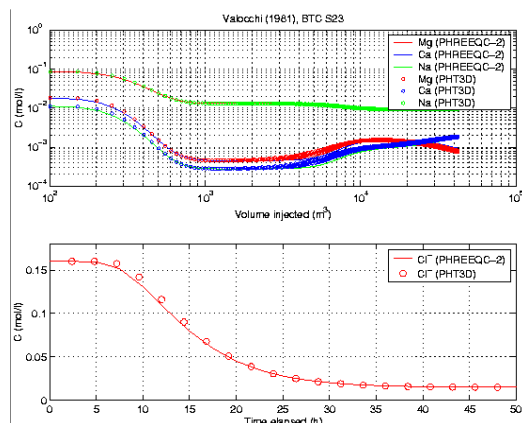


Figure 3. Comparison of simulated chloride and cation concentrations 16 m from the injection point

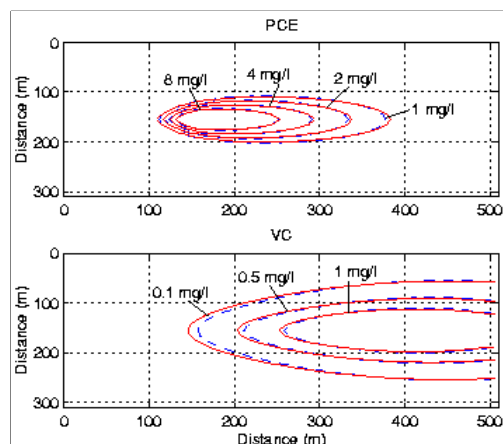


Figure 4. PHT3D simulation (--) of the sequential dehalogenation of PCE in comparison with the solution obtained by RT3D (-).

example. Despite the use of different solution techniques for the kinetic reactions, both solutions agree well. PHT3D was further tested against an analytical solution for arbitrary multi-species sequential/parallel first-order reactions presented by Sun et al. (1999).

SAMPLE 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-

transport of chloride and the transport of three exchangeable heterovalent cations (Mg^{2+} , Ca^{2+} , Na^{+}) undergoing surface reactions. The breakthrough of the injected concentrations at neighboring wells exhibits the chromatographic effects that result from the nonlinear ion-exchange processes. In Fig. 3, breakthrough curves simulated with PHT3D for chloride and for the cations are plotted in comparison with results from a corresponding PHREEQC-2 simulation (Appelo, pers. comm.). Simultaneous dissolution/precipitation and ion-exchanging reactions were verified using a problem presented by Sardin et al. (1986).

Biodegradation

Simulation of transport and reactions of chemicals that undergo biodegradation might be dealt with at different levels of process detail, starting with formulations 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 (e.g., Clement, 1997), explicitly model growth and decay of bacteria (Prommer et al., 2001a) or even take into account the pH-dependency of bacterial growth (Brun and Engesgaard, 2001). Two-dimensional simulation problems presented by Clement (1997) were used to verify kinetic multi-species biodegradation reactions (i) involving sequential first-order degradation of PCE and (ii) for a Monod-type BTEX degradation that uses sequentially a 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. A comparison of PHT3D modeling results (PCE and vinylchloride concentrations after 3 years) in comparison with the solution obtained by RT3D is shown in Fig. 4 for the PCE

Aqueous component	C (initial) (mol l ⁻¹)	Aqueous component	C (initial) (mol l ⁻¹)	Aqueous component	C (initial) (mol l ⁻¹)
S(VI)	5.07×10^{-2}	Ca	1.10×10^{-2}	Mn(2)	9.98×10^{-6}
S(-II)	0.0	Mg	9.83×10^{-4}	Al	4.36×10^{-3}
Fe(II)	3.10×10^{-2}	Na	1.41×10^{-3}	Si	2.11×10^{-3}
Fe(III)	2.02×10^{-7}	K	8.05×10^{-4}	Zn	1.01×10^{-4}
C(IV)	4.92×10^{-4}	Cl	1.21×10^{-4}		

Table 1. Chemical composition of the contaminated groundwater in the sample application.

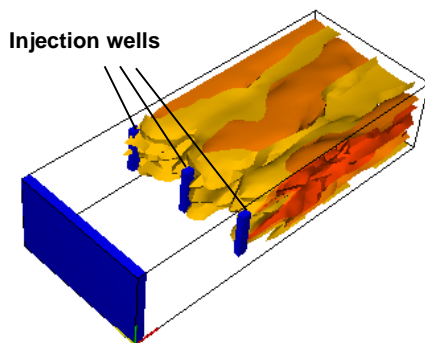


Figure 5. Non-reactive transport in the heterogeneous aquifer.

located at the model boundaries, is 50% of the central well. The results from a non-reactive simulation in which a tracer was injected are shown in Fig. 5. In the reactive transport simulations, acidic leachate (pH = 4.2), including zinc, 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 (see Table 1) as the initial/inflow water but is enriched with an organic substance (Ethanol, C_2H_5OH , 5 mmol/l). The presence of both, sulfate and the degradable organic substance will enable the growth of sulfate reducing bacteria (SRB) in the absence of other, more favorable electron acceptors. As a result of the microbial activity, sulfate is transformed, i.e., reduced, to sulfide which then complexes with zinc and precipitates. As a result of sulfate reduction, the pH of the groundwater increases locally. Fig. 6

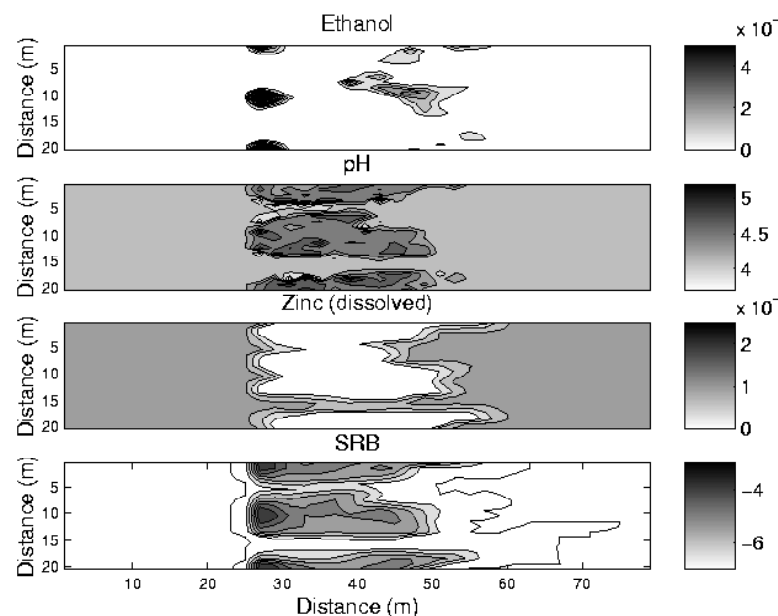


Figure 6. Concentration snapshot for a horizontal plane (Layer 6) of ethanol, pH, zinc and SRB after 50 days simulation time. The concentration unit for ethanol, zinc and SRB is mol/l.

wise injection of a degradable organic substance. After an initial injection for 50 days, injection cycles and cycles of natural groundwater flow alternate every 20 days, creating a transient flow field. During the degradation of the organic substance, a sulfate-reducing environment is created, acting as an in situ reactive zone that will immobilize dissolved metals, i.e., in the case presented here, through precipitation of Sphalerite (ZnS). A hypothetical heterogeneous conductivity distribution creates a non-parallel, three-dimensional flow field that underlies the transport simulations. The model domain ($80\text{ m} \times 21\text{ m} \times 12\text{ m}$) was discretised 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,

remediation (50 days simulation time) for a horizontal plane (Layer 6). Fig. 7 shows a three-dimensional visualization of dissolved zinc concentrations for the same time. 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 transversal dispersive mixing between the injected water and the groundwater passing between the injection wells. With the numerical model, engineering design parameters such as well spacing, (water) injection rates, organic substance concentration and the type of organic substance, i.e., alternative chemicals can be studied and optimized.

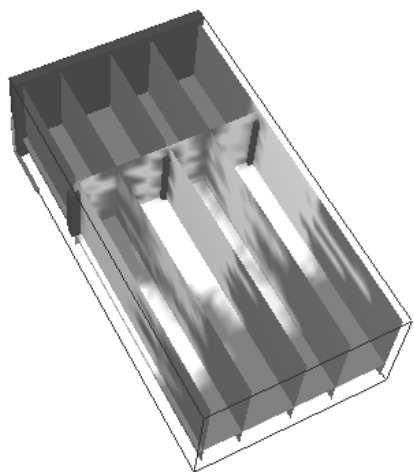


Figure 7. Aqueous zinc concentrations after 50 days simulation time (dark = initial concentration)

SUMMARY

The reactive multi-component transport model PHT3D, its evaluation and a sample application were presented. It has been shown that the model is suitable of 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. Simpler multi-species model applications can be handled easily through pre-defined reaction modules whereas multi-component transport simulations will require users to have a sound understanding of geochemical processes and concepts.

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