Implementation of variably saturated flow into PHREEQC for the simulation of biogeochemical reactions in the vadose zone

L. Wissmeier *, D.A. Barry

Ecole Polytechnique Fédérale de Lausanne (EPFL)
Laboratoire de Technologie Ecologique
Institut d'Ingénierie de l'Environnement
CH-1015 Lausanne, Switzerland

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∗ Author to whom all correspondence should be addressed. Telephone: +41 21 693 5727, facsimile: +41 21 693 5670.

E-mail addresses: laurin.wissmeier@epfl.ch (L. Wissmeier), andrew.barry@epfl.ch (D.A. Barry).

Abstract

A software tool for the simulation of one-dimensional unsaturated flow and solute transport together with biogeochemical reactions in the vadose zone was developed by integrating a numerical solution of Richards' equation into the geochemical modelling framework PHREEQC. Unlike existing software, the new simulation tool is fully based on existing capabilities of PHREEQC without source code modifications or coupling to external software packages. Because of the direct integration, the full set of PHREEQC's geochemical reactions with connected databases for reaction constants is immediately accessible. Thus, unsaturated flow and solute transport can be simulated together with complex solution speciation, equilibrium and kinetic mineral reactions, redox reactions, ion exchange reactions and surface adsorption including diffuse double layer calculations. Liquid phase flow is solved as a result of element advection, where the Darcy flux is calculated according to Richards' equation. For accurate representation of advection-dominated transport, a total-variation-diminishing scheme was implemented. Dispersion was simulated with a standard approach; however, PHREEQC's multicomponent transport capabilities can be used to simulate species-dependent diffusion. Since liquid phase saturation is recalculated after every reaction step, biogeochemical processes that modify liquid phase saturation, such as dissolution or precipitation of hydrated minerals are considered *a priori*. Implementation of the numerical schemes for flow and solute transport have been described, along with examples of the extensive code verification, before illustrating more advanced application examples. These include (i) the simulation of infiltration with saturation-dependent cation exchange capacity, (ii) changes in hydraulic properties due to mineral reactions and (iii) transport of mobile organic substances with complexation of heavy metals in varying geochemical conditions.

Keywords:

reactive transport; unsaturated flow; surface complexation; geochemical modelling; cation exchange; hydraulic properties

Software Availability

Name of software:	RICH-PHREEQ
Developers:	L. Wissmeier and D.A. Barry
Contact information:	EPFL ENAC IIE ECOL, GR A1 475 (Bâtiment GR), Station 2, CH-1015 Lausanne, Switzerland; E-mails: laurin.wissmeier@epfl.ch; andrew.barry@epfl.ch
Hardware requirements:	Platform supporting MS Windows Applications
Software requirements:	PHREEQC (http://www.falw.vu/~posv/phreeqc/download.html or http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html) Windows Script Host
Programming language:	VBScript
Availability and cost:	Available free of charge at http://infoscience.epfl.ch/record/133662

1 Introduction

The vadose zone poses a challenge to soil scientists, hydrologists and environmental engineers in that it combines highly non-linear flow processes with complex biogeochemical reactions. Its vital role as the major life-supporting ecosystem on land is widely recognized. Understanding the interaction of flow and reaction in the unsaturated zone is of importance to quantify limits to its capacities for beneficial use, and to remediate contamination.

Over several decades, many numerical models with sophisticated and efficient algorithms have been developed to solve the governing equations of flow and solute transport (e.g., FEFLOW: Koskinen et al., 1996; MODFLOW: Harbaugh et al., 2000; SUTRA: Voss and Provost, 2008; HYDRUS-1D: Šimůnek et al., 2009). At the same time, flexible software programs for aqueous geochemical reactions evolved and now became standard tools in soil chemistry (e.g., PHREEQC: Parkhurst and Appelo, 1999; ORCHESTRA: Meeussen, 2003; MINTEQ: Gustafsson, 2008). Today's environmental problems of soil degradation, salinisation and pollution with complex organic and inorganic reactants together with novel management and remediation technologies, however, require explicit estimates of interactive flow and reaction processes.

Particularly in the last decade, a new class of computer programs has emerged. These combine sophisticated software packages for flow and transport with geochemical programs to allow for the calculation of complex transient flow fields while preserving the flexibility to simulate a wide variety of geochemical reactions (e.g., MIN3P: Mayer, 1999; LEHGC2.0: Yeh et al., 2001; PHT3D: Prommer et al., 2003; PHAST: Parkhurst et al., 2004; HP1: Jacques and Šimůnek, 2005, Šimůnek et al., 2006b; PHWAT: Mao et al., 2006; CRUNCHFLOW: Steefel, 2007). A disadvantage of coupling otherwise independent programs is the large amount of information that has to be passed between modules. A deeper issue in practice, although not in principle, is the loss of information between modules, leading to difficulties for the transport of pH and redox potential as well as for the influence of reactions on liquid phase saturation. In the following, a scheme is developed that avoids these issues through direct implementation of variably saturated flow and transport into the geochemical modelling software PHREEQC. The scheme and its implementation are referred to as RICH-PHREEQ in this report.

RICH-PHREEQC is the latest development in a series of reactive solute transport models (Prommer et al., 1999; Mao et al., 2006; Brovelli et al., 2009) , that couple liquid phase porous media flow with a detailed description of hydro-geochemical processes on the molecular scale. Previously, we illustrated the implementation of a numerical solution for the moisture-based Richards' equation into PHREEQC (Wissmeier and Barry, 2008). In the present paper, a more versatile approach is used. The mixed form of Richards' equation is employed (Celia et al., 1990), and the applicability of the code is extended to combined saturated (i.e., positive head)-unsaturated conditions and heterogeneous soil profiles, as well as more general boundary conditions. For advection-dominated transport, the implementation of a total-variation-diminishing (TVD) scheme (Gupta et al., 1991) gives accurate results also with sharp concentration fronts.

RICH-PHREEQ is a visual basic script file (VBScript) that creates an input file for simulating saturated-unsaturated flow and geochemical reactions in PHREEQC. Users can edit the VBScript and thereby rapidly develop saturated-unsaturated flow models, upon which arbitrary geochemical reaction models can be built. The structure of the VBScript is discussed in the *User Notes*.

The generated PHREEQC input file typically starts with the definition of initial and boundary solutions (SOLUTION) followed by the various user-defined geochemical reactions (SURFACE, EXCHANGER, EQUILIBRIUM_PHASES etc.). Keywords for visualization (USER_GRAPH) and output of results (SELECTED_OUTPUT, USER_PUNCH) follow. The computations of variably saturated flow and advective-dispersive solute transport are performed entirely in the subsequent USER_PRINT keyword. Changes in element amounts through flow are imposed on the solutions via time-dependent reactions in the KINETICS keywords. The TRANSPORT keyword not only adds the computation of species-dependent diffusion but provides also the general space and time discretisation of the scheme. The implementation at the script level ensures compatibility with future releases of PHREEQC without the requirement for source code maintenance. In addition, the numerical methods are transparent and can be extended by advanced PHREEQC users including those without expert programming knowledge. Specifically, the advantages that arise from the implementation into PHREEQC are (i) direct access to its comprehensive set of geochemical reactions, (ii) direct access to several distributed databases for species definitions, reaction constants and rate definitions, and (iii) the convenience of PHREEQC's graphical user interfaces for the flexible definition of geochemical reactions together with initial and boundary conditions.

The RICH-PHREEQ implementation has a wide range of potential applications. Among these are:

- Evaluation of the sustainability and efficiency of management options for agricultural soils (water holding capacity, nutrient status);
- Risk assessment for waste disposal facilities and drinking water suppliers;
- Evaluation of remediation strategies for contaminated soils such as:
  - Enhanced bioremediation;
  - Surfactant enhanced remediation;
- Simulation of vadose zone constructed wetlands and their treatment efficiency and capacity;

- Evaluation of reactive barriers, their lifetime and potential failures.

In the following, we outline the theoretical background of RICH-PHREEQ before commenting on its numerical implementation. After demonstrating the scheme's accuracy by means of code verification, we will present example applications for (i) cation exchange with saturation-dependent exchange capacity, and (ii) changes in hydraulic properties due to mineral reactions and (iii) transport of a soluble humic substance with multi-site ion complexation according to the diffuse double layer model.

User notes, the VBScript for PHREEQC input file generation, an example simulation and a Matlab® script for result visualization are appended as supplemental online material together with the PHREEQC input files for the simulation example in this paper.

2 Theory

The direct implementation of RICH-PHREEQ without coupling to external software facilitates the *compositional approach* (Panday and Corapcioglu, 1989; Liu et al., 1994) where, in common with traditional approaches, the liquid phase advective flux is calculated from volumetric liquid phase saturation. The liquid phase flux enters in the advection-dispersion equation for solute transport. In contrast to common approaches, mass-conservative liquid phase flow results from the application of the solute transport equation to every element in the solution including oxygen and hydrogen. In addition, this approach leads to an accurate representation of pH, thereby avoiding the need for an artificial "proton excess" master species as suggested by Yeh and Tripathi (1991). At the same time, the distinction between solute and solvent that is usually employed in reactive transport modelling (e.g., Yeh et al., 2001; Steefel, 2007) is avoided. Unlike PHREEQC, RICH-PHREEQ requires strictly charge balanced initial solutions and reactions, which is an acceptable constraint in natural environmental systems.

2.1 Mass balance equation

The general mass balance equation in a one-dimensional soil column that contains multiple phases, which themselves consist of multiple species is given by (e.g., Panday and Corapcioglu, 1989; Lichtner, 1996; Miller et al., 1998; Barry et al., 2002)

$$\frac{\partial}{\partial t}(\theta_\alpha \rho_\alpha \omega_{i\alpha}) = -\frac{\partial}{\partial z}(\theta_\alpha \rho_\alpha \omega_{i\alpha} v_\alpha) - \frac{\partial}{\partial z} j_{i\alpha} + \mathcal{J}_{i\alpha} + \mathcal{R}_{i\alpha} + \mathcal{S}_{i\alpha}, \tag{1}$$

with time t (T), distance downward from the soil surface z (L), volume fraction θ (-), density ρ (M L^{-3}), mass fraction ω, mean pore fluid velocity v (L T^{-1}), non-advective transport j (M L^{-2} T^{-1}), interphase mass exchange $\mathcal{J}$ (M L^{-3} T^{-1}), intraphase reaction $\mathcal{R}$ (M L^{-3} T^{-1}) and external source $\mathcal{S}$ (M L^{-3} T^{-1}). Subscripts α denote phases and i species within phases.

Following Miller et al. (1998) the identities

$$\sum_\alpha \theta_\alpha = 1, \quad \sum_\alpha \mathcal{J}_{i\alpha} = 0, \quad \sum_i \omega_{i\alpha} = 1, \quad \sum_i j_{i\alpha} = 0, \quad \sum_i \mathcal{R}_{i\alpha} = 0, \tag{2}$$

apply to Eq. (1).

Considering a single liquid phase l and an immobile phase s where solution species precipitate, dissolve and adsorb, the phase mass balance is obtained by summing over all species il and is,

$$\frac{\partial}{\partial t}(\theta_l \rho_l) = -\frac{\partial}{\partial z}(\theta_l \rho_l v_l) + \sum_i \mathcal{J}_{il} + \sum_i \mathcal{S}_{il}, \tag{3}$$

$$\frac{\partial}{\partial t}(\theta_s \rho_s) = \sum_i \mathcal{J}_{is} + \sum_i \mathcal{S}_{is}. \tag{4}$$

If there are no external sources, then $\sum_i \mathcal{J}_{il} = -\sum_i \mathcal{J}_{is}$ and Eqs. (3) and (4) can be combined to yield

$$\frac{\partial}{\partial t}(\theta_l \rho_l) = -\frac{\partial}{\partial z}(\theta_l \rho_l v_l) - \frac{\partial}{\partial t}(\theta_s \rho_s). \tag{5}$$

As can be seen from Eq. (5), mineral reactions affect the flow directly by changing phase saturation, but also indirectly through altering constitutive relations (Wissmeier and Barry, 2009).

2.2 Momentum balance/Flow equation for liquid phase

The volume flux q_l of the liquid phase is given by the Darcy equation as

$$\theta_l v_l = q_l = -\frac{k_l}{\mu_l}\left(\frac{\partial}{\partial \mathrm{z}} p_l + \rho_l\right), \tag{6}$$

where k_l (L^2) is the effective permeability, μ_l (M L^{-1} T^{-1}) is the dynamic viscosity and p_l (M L^{-1} T^{-2}) is the fluid pressure (e.g., Hassanizadeh, 1986; Bear and Verruijt, 1987; Bear and Bachmat, 1998).

With θ_l being the volumetric liquid phase saturation, the combination of Eqs. (6) and (5) results in the mixed form of Richards' equation (e.g., Richards, 1931; Klute, 1952; Philip, 1969, 1970; Celia et al., 1990)

$$\frac{\partial \theta_l}{\partial t} = -\frac{\partial}{\partial z}\left[\frac{k_l}{\mu_l}\left(\frac{\partial}{\partial z} p_l + \rho_l\right)\right] - \frac{\partial}{\partial t}(\theta_s \rho_s), \tag{7}$$

where the final term on the right hand side accounts for the influence of mineral reactions on liquid phase saturation.

2.3 Transport equation

Species transport in the liquid phase is given by

$$\frac{\partial}{\partial t}(\theta_l C_{il}) = -\frac{\partial}{\partial z}(q_l C_{il}) + \frac{\partial}{\partial z}\left[\left(D_l^l |q_l| + \theta_l D_{il}^w \tau\right)\frac{\partial}{\partial z} C_{il}\right] + \mathcal{J}_{il} + \mathcal{R}_{il} + \mathcal{S}_{il}, \tag{8}$$

with species concentration C (mol L^{-3}), longitudinal dispersivity D^l (L), molecular diffusion coefficient in free water D^w (L^2 T^{-1}), and tortuosity factor in the liquid phase τ (e.g., Bear, 1972; Bear and Verruijt, 1987; Bear and Bachmat, 1998).

Reaction equations for solution speciation, equilibrium interphase reactions (mineral precipitation/dissolution, ion exchange, surface complexation) and general kinetic reactions in PHREEQC are concisely described by Parkhurst and Appelo (1999). Detailed discussions on the formulation of equations for geochemical reactions are given by Appelo and Postma (2005), Langmuir (1997), Lichtner (1996), Mayer (1999), Steefel (2000, 2007), Stumm and Morgan (1996) and Yeh and Tripathi (1989).

3 Numerical methods

A split-operator approach is employed for the decoupling of simultaneous processes of flow, element transport and geochemical reactions in a discrete time domain. Operator splitting techniques and their performance are described by Barry et al. (1996a; 1996b; 1997; 2000), Kanney et al. (2003), Steefel and Lasaga (1994), Valocchi and Malmstead (1992), Yeh and Tripathi (1989) and Yeh and Tripathi (1991). RICH-PHREEQ uses sequential operator splitting, which provides first-order accuracy with time ($\mathcal{O}(\Delta t)$). The dependency of the introduced splitting error on grid size and time step size for reactions in variably saturated flow conditions was discussed by Jacques et al. (2006).

Fig. 1 near here

RICH-PHREEQ's program flow is illustrated in Fig. 1. A PHREEQC input file is generated using VBScript (Microsoft, 2009), which is run in PHREEQC. Within each time step during the PHREEQC simulation, geochemical equilibrium reactions are calculated followed by kinetic reactions for every cell in the simulation domain. The mass of H_2O and element concentrations are saved. After reaction calculations for all cells, liquid phase flow and solute transport is computed. The rates of changes in element concentrations due to transport are saved and applied as kinetic reactions in the following reaction step.

3.1 Liquid phase flow

For the numerical solution of liquid phase flow the general mass-conservative scheme of Celia et al. (1990) is used. Because flow of a single liquid phase is considered, we omit subscript l for the liquid phase from now on.

Picard iteration together with the Thomas algorithm (Press et al., 1990) was employed to solve the tridiagonal system of nonlinear algebraic equations that results from a second-order, central finite difference space discretisation of pressure heads with a fully implicit time-marching algorithm. Following Šimůnek et al. (2009), discretisation of Eq. (7) leads to

$$\frac{\theta_m^{j+1,k+1}-\theta_m^{j}}{\Delta t}=\frac{1}{\Delta z}\left(K_{m+\frac{1}{2}}^{j+1,k}\frac{h_{m+1}^{j+1,k+1}-h_m^{j+1,k+1}}{\Delta z}-K_{m-\frac{1}{2}}^{j+1,k}\frac{h_m^{j+1,k+1}-h_{m-1}^{j+1,k+1}}{\Delta z}\right)+\frac{K_{m+\frac{1}{2}}^{j+1,k}-K_{m-\frac{1}{2}}^{j+1,k}}{\Delta z}, \tag{9}$$

where K (L T^{-1}) is the unsaturated hydraulic conductivity defined as

$$K=\frac{k}{\mu}\rho g \tag{10}$$

and h (L) is the liquid phase pressure head defined as

$$h=\frac{p}{\rho g}. \tag{11}$$

g is the magnitude of gravitational acceleration (L T^{-2}) and Δz and Δt are numerical cell sizes and time steps, respectively. Subscript m is the cell index and superscripts j and k are indices for time steps and Picard iterations.

Rewriting the left hand side of Eq. (9) as a truncated Taylor series with respect to h around the expansion point $h^{j+1,k}$ leads to

$$\frac{\theta_m^{j+1,k+1}-\theta_m^{j}}{\Delta t}=c_m^{j+1,k}\frac{h_m^{j+1,k+1}-h_m^{j+1,k}}{\Delta t}+\frac{\theta_m^{j+1,k}-\theta_m^{j}}{\Delta t}, \tag{12}$$

where c (L^{-1}) is the specific moisture capacity function defined as

$$c(h)=\frac{d\theta}{dh}. \tag{13}$$

In order to improve convergence in near-saturated conditions our scheme applies an under-relaxation technique to the nodal values of hydraulic conductivity (Paniconi and Putti, 1994; Phoon et al., 2007). Conductivity is therefore calculated as a function of h according to

$$K_m^{j+1,k} = K\left(h_m^{j+1,k}\varpi + h_m^{j+1,k-1}(1-\varpi)\right), \tag{14}$$

where $0 \leq \varpi \leq 1$ is the relaxation factor.

In Eq. (9) the gradient $\frac{\partial K}{\partial z}$ is discretised using internodal conductivities $K_{m+\frac{1}{2}}$ and $K_{m-\frac{1}{2}}$. For most common analytical conductivity models, the use of the geometric mean for the interpolation of internodal conductivities from nodal values K_{i+1}, K_i and K_i, K_{i-1} is superior in resolving sharp moisture fronts compared to other simple weighting methods such as the arithmetic and harmonic mean (Warrick, 1991; Belfort and Lehmann, 2005). Haverkamp and Vauclin (1979) found that the model using the geometric mean as weighting relation is preferable in terms of flexibility, precision, and feasibility for simulating transient water flow in partially saturated soil (see also Zaidel and Russo (1992) for discussion). The influence of conductivity interpolation on the resolution of steep infiltration fronts is illustrated in section 4.1.2. In RICH-PHREEQ, the user can choose between arithmetic, geometric and harmonic mean for the computation of internodal conductivities. The geometric mean is used by default.

For the calculation of water retention and unsaturated hydraulic conductivity the user has the choice between the analytical models by van Genuchten/Mualem (Mualem, 1976; van Genuchten, 1980), Brooks/Corey (Brooks and Corey, 1966) and Fujita/Rogers (Fujita, 1952; Rogers et al., 1983). Other weighting functions for internodal conductivities as well as hydraulic property models can be easily integrated.

As boundary conditions the constant moisture content/constant head, constant flux and free drainage boundaries are implemented. System-dependent boundaries like atmospheric conditions with time series of precipitation and potential evaporation can be simulated as a conditional combination of flux and head boundaries (Šimůnek et al., 2009).

The singularity in q that results from a step-change of the moisture content on a constant moisture boundary leads to false positioning of moisture fronts (Bajracharya and Barry, 1994). The numerical accuracy is improved by using $\theta_0^{j_1}/\theta_0^{j} = 0.5$ (Hildebrand and Cliffs, 1968), where the subscript $m = 0$ denotes the boundary node and j_1 is the first time step after the change in moisture content on the boundary.

3.2 Solute transport

With the definition of chemical elements e as the components of solution species i and constant, species-independent hydrodynamic dispersion, non-reactive solute transport for the liquid phase is described by

$$\frac{\partial M_e}{\partial t} = -\frac{\partial}{\partial z}(qC_e) + \frac{\partial}{\partial z}\left(D^l|q|\frac{\partial}{\partial z}C_e + \theta D_i^w \tau \cdot \frac{\partial}{\partial z}C_i\right). \tag{15}$$

Because C is given in molar concentration M is the moles of an element in the liquid phase. The change in moles of an element with time can be treated as a kinetic geochemical reaction that is conveniently solved by the PHREEQC implemented rate integrator. During the integration of a single time step, the right-hand side of Eq. (15) is treated as a constant. This results in linear convergence of the scheme with Δt, which is consistent with the accuracy of the operator splitting.

Traditionally, solute transport is applied to selected solution species in the aqueous phase only. However, it is recognized that Eq. (15) solves Richards' equation if it is calculated for all aqueous elements since the net non-advective transport is zero according to Eq. (2). With the assumption of constant density, liquid phase flow results from

$$\frac{\partial \theta}{\partial t} = \frac{1}{\rho V_c}\left\{\sum_e \epsilon_e \left[-\frac{\partial}{\partial z}(qC_e) + \frac{\partial}{\partial z}\left(D^l|q|\frac{\partial}{\partial z}C_e\theta\right)\right] + \sum_i \epsilon_i \frac{\partial}{\partial z}\left(D_i^w \tau \cdot \frac{\partial}{\partial z}C_i\right)\right\}, \tag{16}$$

where ϵ is the molar mass (M mol^{-1}) and V_c is the volume of a computational cell.

For the numerical evaluation of the advective flux in Eq. (16), the user has the choice between a first-order upstream weighting scheme and a TVD scheme. In discretised form the first-order scheme is given by

$$\left[-\frac{\partial}{\partial z}(qC)\right]_m^{j+1} = q_{m-\frac{1}{2}}^{j+1}\left[\mathrm{H}\left(q_{m-\frac{1}{2}}^{j+1}\right)C_m^j + \mathrm{H}\left(-q_{m-\frac{1}{2}}^{j+1}\right)C_{m-1}^j\right] - q_{m+\frac{1}{2}}^{j+1}\left[\mathrm{H}\left(q_{m+\frac{1}{2}}^{j+1}\right)C_{m+1}^j + \mathrm{H}\left(-q_{m+\frac{1}{2}}^{j+1}\right)C_m^j\right], \tag{17}$$

where H is the Heaviside function used to distinguish between upward and downward flow (e.g., Wolfram MathWorld, 2008). Indices for elements have been omitted. Internodal fluxes at cell faces are calculated from the liquid phase flow scheme according to

$$q_{m+\frac{1}{2}}^{j+1} = -K_{m+\frac{1}{2}}^{j+1}\left(\frac{h_{m+1}^{j+1} - h_m^{j+1}}{\Delta z} + 1\right). \tag{18}$$

The internodal flux provides the connection between solute transport and the numerical solution of Richards' equation.

Due to explicit time marching for solute transport, the stability of the scheme is restricted to $Cr \leq 1$ (Bear, 1972), where the Courant number Cr is defined by

$$Cr = \frac{q\Delta t}{\theta \Delta z}. \tag{19}$$

Compared to upstream weighting schemes using nodal fluxes (Šimůnek et al., 2009), the present scheme gives more accurate solutions especially in cases where the influent concentration at the boundary is lower than the initial concentration in the column. It is noted, however, that ordinary first-order schemes suffer from severe numerical dispersion, which leads to flawed simulation results for steep concentration gradients in advection-dominated systems (see section 4.2) (Bajracharya and Barry, 1993b, a; Barry and Bajracharya, 1993; Bajracharya and Barry, 1994). Ordinary second- and higher-order schemes perform better in resolving sharp concentration fronts but introduce spurious oscillations, which may result in negative concentrations (Bresler, 1973; Bear and Verruijt, 1987; Rausch, 2005; Bear, 2007). Since PHREEQC simulations fail with negative element concentrations, we abstained from the implementation of ordinary higher-order schemes.

In addition to the upstream weighting scheme, the TVD scheme of Gupta et al. (1991) was implemented. The TVD scheme preserves sharp concentration fronts while maintaining monotonicity of the solution, which is especially relevant in flow situations with high grid Péclet numbers (see section 4.2) (Yee et al., 1985; Cox and Nishikawa, 1991; Moldrup et al., 1994; Ataie-Ashtiani et al., 1996; Oldenburg and Pruess, 2000; Gottlieb et al., 2001; Kadalbajoo and Kumar, 2006). Despite the neglect of the local Courant number in computing the flux limiter, the accuracy of the TVD scheme greatly exceeds the accuracy of commonly applied first- and second-order schemes. The stability of the scheme is restricted to $Cr \leq 0.5$ (Blunt and Rubin, 1992). Fully implicit, unconditionally stable flux limiter schemes are available but necessitate an additional iterative process to evaluate the flux limiter at the new time level (Blunt and Rubin, 1992). This was not followed here as the additional computational burden outweighs the advantage of a further increased accuracy. Furthermore, the time step requirement for the numerical solution of unsaturated flow is usually more restrictive than the grid Courant number.

For the spatial discretisation of the dispersive element flux, given by $\frac{\partial}{\partial z}\left(D^l |q| \cdot \frac{\partial}{\partial z} C_e\right)$ in Eq. (17) a standard second-order finite difference discretisation is employed.

Charge balanced, species-dependent diffusive transport modelled by $\frac{\partial}{\partial z}\left(\theta D_i^w \tau \cdot \frac{\partial}{\partial z} C_i\right)$ can be added to advective-dispersive transport using PHREEQC's multicomponent diffusion capabilities. Tortuosity is then restricted to

$$\theta\tau = \theta^{\varsigma}, \tag{20}$$

where the exponent ς is a free tortuosity parameter (Parkhurst, 2007). Note that for dispersion, elements are transported using the same dispersivity. However, diffusion acts on species with individual diffusion coefficients, which are defined in one of PHREEQC's databases (phreeqd.dat). Obviously, elements need be speciated prior to diffusion calculations.

In a strict sense, water is defined as the solution species H_2O. The volumetric moisture content, θ, however is equal to the sum of the mass of all elements in the liquid phase divided by the liquid phase density and the volume of soil under consideration. For applications where the density of the solution is close to 1 kg dm^{-3} and the contribution of species other than H_2O to the solution volume is negligible, the liquid phase saturation θ can be taken as the mass of H_2O divided by the cell volume. In the present scheme this interpretation of θ is used. However, together with appropriate models for the liquid phase density (e.g., Monnin, 1994), the PHREEQC output of moles of elements as well as species concentrations can be conveniently used to calculate liquid phase density and therefore θ more accurately.

4 Code verification

Because reactions in PHREEQC are well tested, we focus on verification of unsaturated flow and non-reactive solute transport.

4.1 Unsaturated flow

4.1.1 Comparison to the exact solution of Sander et al. (1988)

The simulation of liquid phase flow was validated for a constant flux boundary using the exact solution of Sander et al. (1988). Since the solution is restricted to a certain class of hydraulic models, the hydraulic property functions of Fujita/Rogers (Fujita, 1952; Rogers et al., 1983) were introduced into RICH-PHREEQ. Formulas for water retention and hydraulic conductivity are (Watson et al., 1995):

$$h(\Theta) = h_{air} + \frac{1}{\alpha}\log\left[\frac{(1-\nu)\Theta}{1-\nu\Theta}\right], \tag{21}$$

$$K(h) = K_{sat}\ \exp\left[\frac{K_{sat}(1-\nu)}{D_0}(h-h_{air})\right], \tag{22}$$

with the reduced moisture content Θ defined as

$$\Theta = \frac{\theta-\theta_{res}}{\theta_{sat}-\theta_{res}}, \tag{23}$$

where θ_{sat} and θ_{res} are, respectively, saturated and residual moisture content, h_{air} is the air-entry pressure (L), K_{sat} is the saturated hydraulic conductivity (L T^{-1}), while D_0 (L T^{-1}) and ν are free parameters.

In the exact solution, the initial soil moisture is set to the residual moisture content, $\theta_{ini} = \theta_{res}$. Due to the singularity of $h(\Theta)$ in Eq. (21), the numerical scheme cannot solve for this condition. Therefore, we chose $\theta_{ini} = \theta_{res} + \mathbb{e}$ with $\mathbb{e} > 0$ being small enough to avoid a significant influence on simulation results (Watson et al., 1995). The parameters of the verification are summarized in Table 1, where q_{top} is the constant flux at the top boundary.

Table 1 near here

Fig. 2 near here

Fig. 2 shows excellent agreement between RICH-PHREEQ and the exact solution even for the relatively coarse spatial discretisation and therefore verifies the implementation of the constant flux boundary condition.

4.1.2 Comparison to HYDRUS-1D (Šimůnek et al., 2009)

Verification of infiltration with the Brooks and Corey (Brooks and Corey, 1966) hydraulic model was performed by comparison to HYDRUS-1D for loamy sand (Leij et al., 1997). The hydraulic model is given by:

$$K(\Theta) = K_{sat}\Theta^{\frac{2}{n_{BC}}+l_{BC}+2}, \tag{24}$$

$$\Theta = \begin{cases} |\alpha_{BC}h|^{-n}, & h < -\frac{1}{\alpha} \\ 1, & h \geq -\frac{1}{\alpha}, \end{cases} \tag{25}$$

where α_{BC} (L^{-1}), l_{BC} and n_{BC} are soil parameters. The properties of the simulation are summarized in Table 2.

Table 2 near here

Fig. 3 near here

The results of the verification example in Fig. 3 show that a finer spatial discretisation is necessary in HYDRUS-1D in order to achieve a similar resolution of the sharp moisture fronts. The better performance of RICH-PHREEQ in this special case is due to the use of the geometric mean for the computation of internodal conductivities as opposed to the arithmetic mean used by HYDRUS-1D (see section 3.1). The figure illustrates the general tendency of the arithmetic mean to smooth out sharp infiltration fronts, whereas the geometric mean tends to over-sharpen them. Using the arithmetic average in RICH-PHREEQ, HYDRUS-1D and RICH-PHREEQC give identical results (see section 4.2).

4.2 Solute transport

The performance of the TVD scheme for transport of sharp concentration fronts in transient unsaturated flow conditions was evaluated by comparison to the implicit Galerkin and Crank-Nicholson upstream weighting finite element schemes in HYDRUS-1D.

Flow was calculated using the van Genuchten/Mualem (Mualem, 1976; van Genuchten, 1980) hydraulic model, with

$$\theta(h) = \begin{cases} \theta_{res} + \dfrac{\theta_{sat} - \theta_{res}}{[1 + (\alpha_{GM} h)^{n_{GM}}]^{m_{GM}}}, & h < 0 \\ \theta_{sat}, & h \geq 0 \end{cases}, \tag{26}$$

$$K(h) = K_{sat} \Theta^{l_{GM}} \left[1 - \left(1 - \Theta^{\frac{1}{m_{GM}}} \right)^{m_{GM}} \right]^2, \tag{27}$$

where α_{GM} (L^{-1}), n_{GM}, m_{GM} and l_{GM} are soil parameters. The top boundary was set to a constant moisture content/constant concentration boundary with θ_{top} and C_{top}, respectively. The initial solute concentration is C_{ini}. For better comparability with HYDRUS-1D, the computation of internodal conductivity in RICH-PHREEQ was set to arithmetic averages. The parameters of the simulation are summarized in Table 3.

Table 3 near here

Fig. 4 near here

The perfect agreement of moisture contents computed with HYDRUS-1D and RICH-PHREEQ is shown in Fig. 4a. The location of the plane of separation, z_{ps}, between event and pre-event water is calculated according to (Katou et al., 2001)

$$\int_0^{z_{ps}} \theta \, dz = \int_0^{\infty} \theta - \theta_{ini} \, dz. \tag{28}$$

The plane of separation gives the theoretical position of an influent concentration front for a non-reactive solute where the initial pore water is completely replaced by the influent solution without mixing or hydrodynamic dispersion. In Fig. 4a it is denoted by a dashed vertical line at $z_{ps} = 3.5$. The right hand side of Eq. (28) is represented by the upward hatched area (/) whereas the left hand side is represented by the downward hatched area (\). The upward and downward hatched areas overlap in the crossed area.

Fig. 4b shows the concentration profiles as calculated by HYDRUS-1D together with the TVD scheme in RICH-PHREEQ. The explicit upstream weighting finite difference scheme in RICH-PHREEQ gives very similar results to the upstream weighting finite element scheme in HYDRUS-1D and is therefore not displayed. The figure illustrates the superior performance of the TVD scheme compared to the second- and first-order schemes, by reproducing the theoretical position of the half concentration $z\left(\frac{C_{top}-C_{ini}}{2}\right) = z_{ps}$, avoiding spurious oscillations and significantly reducing numerical dispersion. Therefore, the TVD scheme accurately simulates the sharp interface between event and pre-event water in advection-dominated flow conditions. Due to the simplifications of the scheme (see section 3.2 for details), the concentration gradient shows a limited amount of artificial dispersion. However, in contrast to the upstream weighting scheme, concentration gradients are not further reduced at later times but remain constant.

5 Example applications

The application examples in this section are simulated with small adaptations of RICH-PHREEQ, which can be easily followed by the users familiar with PHREEQC.

5.1 Saturation-dependent exchange capacity

In this example, we investigate a cation exchange process in a soil with variable exchange capacity, in particular its influence on the solution composition of an infiltrating moisture front. The simulation is motivated by the consideration that exchange sites in the dry pore-space do not participate in the exchange process until the liquid phase saturation rises, the pore-space becomes saturated and the sites are activated. The simulation was carried out for an initially dry soil column of sandy clay loam (Leij et al., 1997) where the residual soil moisture contains a sodium carbonate (Na_2CO_3) solution. The exchange sites, both active and inactive, are thus entirely filled by sodium. From the top end, a calcium chloride ($CaCl_2$) solution infiltrates the soil column at low constant flux, thereby increasing the moisture content and cation exchange capacity. The properties of the simulation are summarised in Table 4.

Table 4 near here

For simplicity, a linear relation between moisture content and the amount of exchange sites was used. A direct relation between the number of exchange sites and the wetted surface area can be implemented through models that compute wetted surface area with moisture saturation (e.g., Taylor and Jaffe, 1990). However, the linear relation to moisture content can be used as a first approximation and guideline for more sophisticated model development. The amount of accessible exchange sites was set to 5.55×10^{-2} meq kg_{H2O}^{-1}.

Fig. 5 near here

Fig. 5a illustrates the progressing moisture front after 10, 25 and 50 h. Fig. 5b shows the exchanger composition in milliequivalents. As expected the active exchange capacity (sum of equivalents of exchange species) closely follows the behaviour of moisture content profiles. Solution concentrations of cations are displayed in Fig. 5c. Because anion transport is unaffected by cation exchange anion concentrations are omitted. Profiles of sodium concentrations clearly show a snowplough effect, where previously adsorbed sodium is exchanged for the infiltrating calcium that has a higher concentration and higher preference for the exchange sites. Consequently, concentrations of desorbed sodium develop a characteristic peak, which by far exceeds the initial and influent concentrations (Barry et al., 1983; Bajracharya and Barry, 1993a, 1995).

With a 50-fold higher input of equivalents of calcium compared to the total exchange capacity the retardation of the calcium concentrations is insignificant. From Fig. 5b it can be seen that the exchange front, where sodium is released from the exchanger and replaced by calcium, coincides with the arrival of the dispersed calcium front. Nevertheless, the moisture front is still ahead of the exchange front. Accelerated moisture movement is due to the initial soil moisture that is mobilized by the infiltrating solution and pushed ahead of the event water, as demonstrated in section 4.2. In this case, the rise of active exchange capacity behind the exchange front accompanied by continued desorption of sodium causes the skewed shape of the sodium peak. For steep moisture fronts and high initial moisture contents the retardation of the exchange front behind the moisture front results in an insignificant rise of exchange capacity behind the exchange front, which is why under these conditions moisture-dependent exchange can be ignored.

5.2 Dynamic hydraulic properties

This example illustrates an extension of RICH-PHREEQ for simulating the effect of mineral reactions on unsaturated hydraulic properties in variably saturated flow conditions. The model equations for the dynamic adjustment of parameters in the hydraulic functions were derived in Wissmeier and Barry (2009). The model is based on the conversion between water retention and pore size distribution via the Young-Laplace equation and implements a thermodynamically sound adjustment of pore-size distributions due to precipitation/dissolution reactions. In order to avoid further complications, the change in mineral volume ΔV_M (L^3 L^{-3}) is translated to the entire pore-size distribution without respecting the fact that part of the pores in the distribution may be dry and therefore unaffected by mineral reactions. Together with the van Genuchten/Mualem hydraulic model, the following model equations apply:

$$\theta_{sat}^{*} = \theta_{sat} - \Delta V_M \tag{29}$$

$$\alpha_{GM}^{*} = \alpha_{GM} \left(\frac{\theta_{sat}^{*} - \theta_{res}}{\theta_{sat} - \theta_{res}}\right)^{\frac{1}{3}} \tag{30}$$

$$K_{sat}^{*} = K_{sat} \frac{\sqrt{\theta_{sat}^{*}}\,(\alpha_{GM}^{*})^2\,(\theta_{sat}^{*} - \theta_{res})^2}{\sqrt{\theta_{sat}}\,\alpha_{GM}^2(\theta_{sat} - \theta_{res})^2}, \tag{31}$$

where * denotes adjusted hydraulic parameters after mineral reactions. Wissmeier and Barry (2009) provide a detailed discussion of the effect of mineral reactions on the hydraulic parameters of the van Genuchten/Mualem model in variably saturated conditions.

The following simulation is motivated by the frequently observed permeability reduction in reactive barriers, where minerals precipitate due to adsorption-desorption processes (Li et al., 2006; Parbs et al., 2007). In this case, a natron-saturated (Na_2CO_3) solution infiltrates into a calcite-saturated ($CaCO_3$) sandy clay loam (Leij et al., 1997) that contains a high-capacity cation exchanger at 2 cm depth whose sites are initially filled with calcium. Upon arrival of the infiltration front at the exchange layer, sodium ions exchange with adsorbed calcium due to their high concentration and increase calcium concentrations in solution. Because of the large abundance of carbonate, calcite becomes supersaturated and precipitates following the exchange process. The precipitation of calcite leads to a reduction in the saturated moisture content and saturated conductivity but at the same time in a decrease of the van Genuchten parameter α_{GM}. The properties of the simulation are summarized in Table 5.

Table 5 near here

Fig. 6 near here

The results in Fig. 6 show the combined effect of cation exchange and mineral precipitation on the moisture profile of the infiltration front. The growing discontinuity in moisture content results from the discontinuous hydraulic properties that follow calcite precipitation.

Solution concentrations show strong retardation compared to the moisture front caused by (i) the exchange process with extremely high exchange capacity and (ii) the significant initial soil moisture. The pH profiles illustrate the high pH of the infiltrating (pH 11.5) and initial (pH 9.9) solutions but also the decline due to calcite precipitation. Sodium and carbonate have similar concentration profiles. However, sodium is taken up from the free solution by exchange whereas carbonate is precipitated as calcite as a consequence of exchange.

Fig. 7 near here

The results in Fig. 7 illustrate the development of the hydraulic parameters that accompany the precipitation of calcite. The decrease in saturated moisture content θ_{sat} reflects directly the volume of precipitated calcite according to Eq. (29). Together with decreasing pore volume, saturated conductivity as well as the van Genuchten parameter α_{GM} are decreasing. The exchanger compositions that results from Na/Ca exchange are displayed in the two lower graphs. Their profiles show that despite the larger preference for divalent ions, calcium is completely removed from the exchanger due to the large abundance of sodium in the infiltrating solution.

This simulation demonstrates the flexibility of RICH-PHREEQ to incorporate changes in flow properties due to mineral reactions. The simulation shows the importance of the mutual influence of flow and reaction, where flow sustains equilibrium reactions that lead to changes in hydraulic properties and therefore influence back on flow dynamics.

An implication for the design of reactive barriers that results from this simulation could be that the adsorbing substrate is pre-washed with a solution of similar major ion content compared to those expected in field conditions in order to avoid large concentration contrast between the ions in the infiltrating solution and the exchanger.

5.3 Transport of organic complexes

Humic substances act as important chelating agents in natural environments. Due to their complexing properties, soluble humic substances retain and transport heavy metals in the unsaturated zone via colloid-facilitated solute transport (Carrillo-González et al., 2006; Šimůnek et al., 2006a). In addition, they facilitate the biological uptake of trace metals and other cations by several mechanisms, one of which is preventing their precipitation; another seems to be a direct and positive influence on their bioavailability (Senesi, 1992; von Wandruszka, 2000). In this example, we illustrate the release of complexed cadmium from a soluble humic substance due to changing geochemical conditions during an infiltration event. The organic substance is conceptualized as an assembly of mobile surfaces that contains 20 different site types for mono and bidendate metal binding according to the WHAM submodel V (Tipping, 1992, 1993). By including protonation/deprotonation reactions and electrostatic forces the pH and ionic strength dependence of association reactions is considered (Dzombak and Morel, 1990). In addition to complexation, ions in the solution are bound to the sorption sites' diffuse layer whose composition is calculated explicitly using a fixed Donnan volume (Parkhurst and Appelo, 1999). The explicit calculation of ions in the diffuse layer is required by the charge balance constraint. In contrast to more sophisticated colloid transport models (Penrose et al., 1990; Šimůnek et al., 2006a; Bradford and Torkzaban, 2008; Flury and Qiu, 2008), we assume conservative transport of the organic substance.

The influent solution that enters the domain with a constant flux of 0.01 cm min^{-1} contains 1 µmolal $CdCl_2$ together with 0.0466 kg m^{-3} of the humic substance. The humic substance is composed of 3.97456×10^{-5} moles of sorption sites with a site density of 46,500 m^2 g^{-1} (Appelo, 2009). The surface assembly is initially in equilibrium with the influent solution. At a depth of 2 - 6 cm the sandy clay loam (Leij et al., 1997) is amended with gypsum as a solid phase, which is allowed to equilibrate with the soil solution. The parameters of the simulation are given in Table 6.

Table 6 near here

Fig. 8 near here

The column profiles in Fig. 8a show the progressing moisture front together with pH. In the profile, after 40 min a pronounced pH peak has developed directly ahead of the solute front. The influence of the gypsum layer at 2 cm is still negligible. Since there is pure pre-event water in the upper 2 cm, the pH peak is purely a result of diffusion/dispersion of the influent solution. A pH change of similar magnitude is observed when diluting the initial humic solution with pure water in a simple batch simulation. This demonstrates the effect on ionic strength and absolute solution concentration of surface complexes. When the solution reaches the gypsum layer, its pH drops because free calcium is adsorbed to the humics. The latter process is accompanied by releases of protons from surface functional hydroxyl groups. Fig. 8b displays concentrations of calcium and cadmium in the solution. At the initial moisture content, water fluxes are negligible and thus the solutes are immobile. As a result, increased calcium concentrations appear behind the gypsum layer only at the latest profile after 200 min when the moisture front has passed. When the humic substance enters the gypsum layer, the competition with calcium for the adsorption sites leads to a strong release of previously complexed cadmium. Calcium is provided by the dissolution of gypsum at concentrations that are 1.5×10^4 times larger than the initial cadmium concentration. Fig. 8c shows concentrations of chloride and the humic substance, which are both unaffected by complexation and mineral dissolution. Fig. 8d displays amounts of cadmium and calcite that are bound to the mobile organic substance. The graph clearly shows the change from purely cadmium-filled sites to calcium-dominated sites despite the sites' larger preference for cadmium. However, the total moles of complexed ions decrease because of the lower pH. Fig. 8e shows the large amount of calcium in the electric double layer (EDL) compared to complexed calcium. Due to the large abundance of calcium in the gypsum layer, the fraction of cadmium in the diffuse layer declines. Together with ionic strength, Fig. 8f shows the negative charge in the EDL that counterbalances the overall positive charge of the complexes. With increasing calcium concentration in the gypsum layer, the charge in the diffuse layer decreases and indicates an increasing number of positively charged complexes.

This example illustrates the capability of RICH-PHREEQ to simulate complexation according to the diffuse double layer model by Dzombak and Morel (1990) together with unsaturated flow. In addition, it shows the scheme's flexibility in defining mobile adsorbents such as surfaces and ion exchangers. The simulation illustrates how heavy metals can be complexed by organic substances and re-enter the free solution through changing geochemical conditions, where they pose a potential threat to the aquatic ecosystem. It is shown that the humic substance carries a positive charge in the given geochemical setting. Therefore, electrostatic attraction may lead to additional reactions such as colloid adsorption in soils with high immobile cation exchange capacity. The adsorption process can be included in the simulation by defining additional reactions between the mobile adsorption sites and the immobile exchanger. In addition, processes such as attachment/detachment and straining/wedging also result in non-conservative transport of the humic substance (McGechan and Lewis, 2002; Flury and Qiu, 2008). In principle, RICH-PHREEQ allows for the extension to a full colloid-facilitated transport similar to that published by Šimůnek et al. (2006a). However, this example is intended to indicate the capabilities of RICH-PHREEQ without large modifications of the original scheme.

6 Concluding remarks

RICH-PHREEQ solves for advective-dispersive transport of chemical elements (rather than species), where the Darcy flux is calculated from a standard numerical solution of the mixed form of Richards’ equation. The verification examples demonstrate the accurate simulation of liquid phase flow that results from transporting the entire ensemble of elements in the solution. The explicit TVD scheme for advective solute transport increases the accuracy of scheme at high grid Péclet numbers by transporting elements with negligible numerical dispersion. Species-dependent diffusion can be included by making use of PHREEQC’s multicomponent transport capabilities and associated databases for diffusion coefficients.

Before every transport step, the moisture saturation of the soil is recalculated from the mass of the solution constituents, which may change during the course of reaction calculations. Unlike existing software, our implementation considers moisture content-modifying reactions, such as dissolution and precipitation of hydrated minerals. The influence of biological activity on the liquid phase saturation and composition can be incorporated using appropriate stoichiometric reaction expressions. Since PHREEQC for Windows (Post, 2009) explicitly calculates the solution density from the ion size database by Millero (2000), the extension of RICH-PHREEQ to density-dependent unsaturated flow where the solution density changes due to geochemical reactions is envisaged.

The scope of RICH-PHREEQ is similar to HP1, which is a coupling of HYDRUS-1D and PHREEQC (Jacques and Šimůnek, 2005; Šimůnek et al., 2006b). However, the presented scheme is based on a different approach and thereby produces some beneficial features by comparison:

- Easy extendibility due to implementation on a script level;
- Choice of standard weighting schemes for the computation of internodal conductivities;
- *A priori* consideration of moisture content modifying reactions;
- Accurate simulation of advection-dominated transport; and
- Compatibility with future releases of PHREEQC without additional maintenance.

Compared to other integrated codes for unsaturated reactive flow RICH-PHREEQ has the key advantage of direct access to all PHREEQC reactions.

Disadvantages of RICH-PHREEQC are long computation times that could be significantly reduced by implanting an adaptive time-stepping procedure, and the lack of a graphical user interface for user-friendly setup of liquid phase flow.

Nevertheless, RICH-PHREEQ offers a valuable tool for the simulation of non-standard problems of flow and reaction in the vadose zone. The examples show cases that can be simulated with RICH-PHREEQ with only minor modifications but are beyond the scope of HP1 or, to the authors' knowledge, any other model for flow and reaction in the vadose zone.

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