# *Simulation Tool for Variably Saturated Flow with Comprehensive Geochemical Reactions in Two- and Three-Dimensional Domains*

L. Wissmeier*, D.A. Barry

Ecole Polytechnique Fédérale de Lausanne (EPFL)

Laboratoire de Technologie Ecologique

Station 2, CH-1015 Lausanne, Switzerland

Resubmitted on 17 August 2010 to Environmental Modelling & Software

* Author to whom all correspondence should be addressed. Telephone: +41 21 693 5727, facsimile: +41 21 693 8035

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

## Abstract

We present a software tool for simulations of flow and multi-component solute transport in two and three-dimensional domains in combination with comprehensive intra-phase and inter-phase geochemistry. The software uses IPhreeqc as a reaction engine to the multi-purpose, multidimensional finite element solver COMSOL Multiphysics® for flow and transport simulations. Here we used COMSOL to solve Richards' equation for aqueous phase flow in variably saturated porous media. The coupling procedure presented is in principle applicable to any simulation of aqueous phase flow and solute transport in COMSOL. The coupling with IPhreeqc gives major advantages over COMSOL's built-in reaction capabilities, i.e., the soil solution is speciated from its element composition according to thermodynamic mass action equations with ion activity corrections. State-of-the-art adsorption models such as surface complexation with diffuse double layer calculations are accessible. In addition, IPhreeqc provides a framework to integrate user-defined kinetic reactions with possible dependencies on solution speciation (i.e., pH, saturation indices, and ion activities), allowing for modelling of microbially mediated reactions. Extensive compilations of geochemical reactions and their parameterization are accessible through associated databases.



## Keywords

Geochemistry, Reaction, PHREEQC, IPhreeqc, Richards' Equation, Unsaturated Flow, COMSOL, Solute Transport


## Research highlights

- Coupling of COMSOL and PHREEQC facilitates simulation of variably saturated flow with comprehensive geochemical reactions.
- The use of finite elements allows for the simulation of flow and solute transport in complex 2 and 3D domains.
- Geochemical reactions are coupled via sequential non-iterative operator splitting.
- The software tool provides novel capabilities for investigations of contaminant behaviour in variably saturated porous media and agricultural management.

## Software requirements

COMSOL Multiphysics® including Earth Science Module (tested version: 3.5a; due to a memory leak in versions 4.0 and 4.0a, these are not suitable for the presented coupling) Price for single user academic license including Earth Science Module ca. 2000 €

Matlab® (tested versions: 7.9, 7.10) Price for single user academic license including Parallel Computing Toolbox ca. 650 €

IPhreeqc (COM-version, available free of charge at http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/)

The coupling files together with animations of the presented simulations are available at http://infoscience.epfl.ch/record/143469 (link: download fulltext)

# 1 Introduction

Computer simulations of water availability and quality play an important role in state-of-the-art water resources management and agriculture (Barry, 1992; Šimůnek and Bradford, 2008). Due to the importance of the unsaturated zone as the major life-supporting ecosystem on land (Brussaard et al., 2007), there is a great demand for understanding and predicting the complex interactions between highly non-linear vadose zone flow and bio-geochemical reactions (Wissmeier et al., 2009). However, many of the most utilized software programs focus either on physical flow and transport phenomena (e.g., MODFLOW (Harbaugh et al., 2000), SUTRA (Voss and Provost, 2008), HYDRUS (Šimůnek et al., 2009)), or on geochemical reactions (e.g., MINTEQ (Gustafsson, 2010), CHESS (van der Lee, 1998), ORCHESTRA (Meeussen, 2003)). Saturated flow codes have been coupled with geochemical reaction packages to produce combined water flow, multispecies transport and complex geochemical reactions (e.g., PHT3D (Prommer et al., 1999), DART (Freedman and Ibaraki, 2002), PHAST (Parkhurst et al., 2004), PHWAT (Mao et al., 2006). In recent years, simulation tools for unsaturated porous media flow with detailed geochemistry have emerged (HP1 (Šimůnek et al., 2009), RICH-PHREEQ (Wissmeier and Barry, 2010)). Although powerful tools, the applicability of the aforementioned unsaturated flow/transport/reaction models is restricted to systems with one-dimensional movement of water and solutes.

The coupling of COMSOL (COMSOL Multiphysics®, 2010) and IPhreeqc (Charlton and Parkhurst, 2010) presented here extends the capabilities of these models by combining unsaturated porous media flow in two and three dimensions with comprehensive geochemical reactions. IPhreeqc is a version of PHREEQC (Parkhurst and Appelo, 1999) that is specifically designed for coupling to multicomponent transport simulators. While it retains all of PHREEQC's reaction capabilities, IPhreeqc provides additional methods for data manipulation and communication to the host application. The coupled model's main features are listed below.

Unsaturated Flow:

- Constitutive relations according to van Genuchten (1980), Brooks and Corey (1964) or user-defined
- Anisotropic unsaturated conductivity

- Specific storage according to fluid compressibility or user-defined storability function
- Fluid density, viscosity and liquid source term through user-defined expressions with possible dependencies on COMSOL variables

Multispecies Solute Transport:

- Dispersivity in directions parallel and orthogonal to flow
- Tortuosity according to Millington and Quirk (1961) or user-defined
- Species independent coefficient of molecular diffusion and dispersivities
- Liquid source concentrations and solute sources through user-defined expressions with possible dependencies on COMSOL variables

Geochemical Reactions:

- Equilibrium solution speciation and redox reactions
- Equilibrium mineral dissolution/precipitation
- Ion exchange on permanently charged adsorption sites
- Surface adsorption according to the diffuse double layer model (Dzombak and Morel, 1990) or the CD_MUSIC model (Hiemstra et al., 1989) with or without explicit calculation of the diffuse double layer composition
- Kinetic reactions according to user-defined rate equations, with possible dependencies on solution speciation, temperature or moisture content
- Gas phase exchange
- Solid solutions

A considerable advantage of the coupling results from the flexibility of COMSOL to define any input parameter as a function of internal variables. For example, root water uptake, entered as a negative liquid sources term, can be defined by a function of space coordinates and liquid phase pressure head. In addition, IPhreeqc's capabilities to integrate user-defined rate expressions allows for the simulation of complex time-dependent geochemical reactions with explicit dependencies on solution speciation (e.g., ion activities, pH, mineral saturation). With these capabilities, the presented model is significantly more comprehensive than existing codes in the field of unsaturated reactive transport modelling, such as MIN3P (Mayer et al., 2002) and RETRASO (Saaltink et al., 2004). The model setup is greatly facilitated by graphical user interfaces for flow and transport (COMSOL) and reactions (PHREEQC).

This paper is organized as follows. Section 2 briefly describes the underlying theory of component-based phase flow, section 3 illustrates the coupling procedure, and sections 4 and 5 provide application examples for kinetic pesticide degradation and fertigation via a subsoil drip irrigation system (files for these cases are available for download).

## 2 Theory

In the presented scheme, the classical advection diffusion/dispersion equation was used for multi-component solute transport (Bear, 1972, 2007; Bear and Bachmat, 1998),

$$\frac{\partial \theta c_i}{\partial t} = -\nabla \cdot (\boldsymbol{q} c_i) + \nabla \cdot \left(\theta \bar{\bar{\boldsymbol{D}}} \boldsymbol{\nabla} c_i\right), \tag{1}$$

where θ is the relative liquid phase saturation (m$^3$ m$^{-3}$), $c_i$ (kg m$^3$) is the concentration of solution species $i$, $\boldsymbol{q}$ (m s$^{-1}$) is the Darcy flux and $\bar{\bar{\boldsymbol{D}}}$ (m$^2$ s$^{-1}$) is the hydrodynamic dispersion tensor.

Recognizing that the liquid phase is composed of solution species according to

$$\theta = \frac{\sum_i n_i m_i}{\rho}, \tag{2}$$

where $n_i$ (mol m$^3$) is the moles of solution species $i$ in a control volume with a molar weight $m_i$ (kg mol$^{-1}$), the application of Eq. (1) to all solution species in the liquid phase effectively yields phase mass balance according to

$$\frac{\partial \rho\theta}{\partial t} = -\nabla \cdot \rho\theta\boldsymbol{v}, \tag{3}$$

where $\boldsymbol{v}$ is the barycentric mass flow velocity of the liquid phase (Corey and Auvermann, 2003). This implies that the net mass flux induced by diffusion/dispersion (Letey et al., 1969) can be neglected , which is a common assumption (Jacques and Šimůnek, 2010; Miller et al., 1998; Šimůnek et al., 2006; Šimůnek et al., 2009).

In the presented scheme, the Darcy flux $\boldsymbol{q} = \boldsymbol{v}\theta$ (m s$^{-1}$) in is computed from Richards' equation according to

$$\boldsymbol{q} = \frac{\overline{\overline{\boldsymbol{K}}}}{\rho g}(\boldsymbol{\nabla} p + \rho g \boldsymbol{\nabla} z), \tag{4}$$

(e.g., Bear, 1972, 2007), where $\overline{\overline{\boldsymbol{K}}}$ is the unsaturated hydraulic conductivity tensor (m s$^{-1}$), $p$ is the fluid pressure (kg m$^{-1}$ s$^{-2}$) and $g$ is the magnitude of gravitational acceleration (m s$^{-2}$).

The other major part of the model concerns geochemical reactions (including biological reactions modelled using a geochemical approach). Thorough descriptions of the models for this part are available in textbooks (Appelo and Postma, 2005; Langmuir, 1997) and the PHREEQC manual (Parkhurst and Appelo, 1999).

## 3 Coupling procedure

In the discretized time domain of the numerical model, the three simultaneous and dependent processes *flow*, *solute transport* and *reaction* are separated using a non-iterative sequential split-operator approach where $\Delta t$ is the length of the coupling time step. The coupling time step is further reduced within the iterative schemes for unsaturated flow, solute transport and geochemical speciation as required by the respective algorithms. As result of the decoupling, concentrations are assumed independent of reactions in solute transport computations. As well, the liquid phase saturation and density are similarly assumed independent of concentrations and reactions during flow calculations. During the geochemical reaction step (performed within IPhreeqc), the solution composition is assumed independent of both flow and transport. The influence of reaction kinetics, grid size and splitting time step on the introduced splitting error in unsaturated flow situations was investigated by Jacques et al. (2006). General discussions on operator splitting are provided by Yeh and Tripathi (1989), Valocchi and Malmstead (1992) and Barry et al. (2000; 1996; 1997), among others.

**Fig. 1. Program flow and structure.**

Fig. 1 illustrates the program structure for the coupling of COMSOL and IPhreeqc using Matlab (Matlab®, 2010) as the controlling application and interface for the COMSOL and IPhreeqc modules (grey shaded, dashed boxes). The code is organized in three major m-files (black textboxes in Fig. 1). At the beginning of the simulation, the controlling script *coupling_COMSOL_PHREEQC.m* runs subscripts to configure the simulation domain with flow and transport properties, initializes COMSOL and IPhreeqc computations and specifies boundary conditions. Geochemical properties such as pH and redox potential (pe) are extremely sensitive to the total element concentrations. Minimal deviations of the ratio of oxygen to hydrogen from the stoichiometric ratio of 1:2 in the simulation of pure water will dramatically affect the pe, for example. Precise concentration values for initial and boundary conditions in COMSOL are thus conveniently determined by preliminary PHREEQC speciation calculations.

After the initialization procedure, computations enter the iteration loop of the split operator, where COMSOL and IPhreeqc procedures alternate for the calculation of flow, transport and reactions. Data from the output of one procedure is passed back to the Matlab workspace and reformatted for the following procedure using the functions *phreeqc2comsol* and *comsol2phreeqc*. For the computation of aqueous phase flow in COMSOL, fluid pressures are calculated from the output of the preceding reaction step (mass of solution in control volume, solution density, pressure-saturation relation). Darcy flux velocities from flow calculations together with master species concentrations from the reaction step are input into the COMSOL solute transport routine (Eq. (1)). The use of master species instead of solution species considerably reduces the degrees of freedom in transport calculations and therefore the numerical burden (Steefel and MacQuarrie, 1996). However, it impedes the simulation of species-dependent diffusion. The *comsol2phreeqc*-function retrieves the results from COMSOL as a vector of all degrees of freedom (fluid pressure and element concentrations) at all nodes in the domain. The vector is reformatted as a numeric Matlab array. Master species concentrations from transport calculations are multiplied by moisture contents from flow calculations. This yields the aqueous phase composition at each node in terms of moles of master species per control volume. In the IPhreeqc reaction step, each node in the simulation domain is represented by a single batch reactor that contains physical amounts (moles) of solution elements, minerals, gases and adsorption sites. Since only the liquid phase composition is altered through flow and transport, *comsol2phreeqc* only updates the solution composition using IPhreeqc's method *SOLUTION_MODIFY.* From the ensemble of elements, the aqueous solution is speciated, and mineral reactions, surface adsorption/desorption reaction and kinetic reactions are computed. After the IPhreeqc reaction procedure, flow and transport calculations in COMSOL are reinitialized with the updated values of moisture content and master species concentrations using the *phreeqc2comsol*-function. Results, which are passed back from IPhreeqc to the Matlab workspace as a cell array, are reshaped as a vector with the same structure of the COMSOL solution vector. COMSOL's *asseminit*-function is used to create valid initial conditions for flow and transport calculations in COMSOL.

**All** primary master species in the liquid phase (including elemental oxygen and hydrogen) must be included in solute transport calculations in order to represent flow by the transport of liquid phase components. This approach has been applied in previous couplings of geochemistry in PHREEQC with unsaturated flow and transport calculations (Jacques et al., 2008; Wissmeier and Barry, 2010). Charge imbalance, present in initial and boundary solutions or developing during reactions (e.g., surface adsorption without explicit calculation of the diffuse layer composition) (Parkhurst, 2010), is treated as an extra solution component in transport calculations. It is also included in speciation calculations in order to accurately reproduce pH and pe.

During the conversion from units relative to an arbitrary control volume in COMSOL (e.g., $m^3\ m^{-3}$ for $\theta$) to physical quantities in IPhreeqc, the size of the batch reactors is taken as one litre for convenience. Thus, solid phase properties in IPhreeqc, such as the moles of adsorption sites and mineral phases have to be understood as per litre of unsaturated zone volume (soil including pore space). Without further modifications, solid phase properties are independent of water contents, i.e., the moles of mineral phases or exchange sites in contact with the unsaturated soil solution do not change due to changes in moisture contents.

Negative master species concentrations may result from oscillatory behaviour of COMSOL's finite element scheme for solute transport in the vicinity of sharp concentration gradients. The performance index, defined as the product of the grid Péclet number and the Courant number, can be used as an indicator of oscillatory transport behaviour (Huyakorn and Pinder, 1983; Perrochet and Berod, 1993; Šimůnek et al., 2009). Since IPhreeqc defines the solution composition in terms of moles of elements, negative concentrations from the

COMSOL-procedure are set to zero during reaction calculations. After the reaction step, negative concentrations from the previous flow/transport step in COMSOL are summed to the master species concentrations that are output of IPhreeqc. The summation of negative concentrations from transport simulations to the results from reaction calculations avoids significant mass balance errors that would otherwise result from the repeated adjustment of negative output from COMSOL to zero. This procedure remedies mass balance errors. Nevertheless, it is recommended to avoid oscillations in solute transport through appropriate domain discretisation (Donea and Huerta, 2004; Perrochet and Berod, 1993).

For accurate transport of pH in unbuffered solutions, the relative tolerance of the solute transport scheme in COMSOL is set to $10^{-10}$. In order to decrease the absolute tolerance for oxygen and hydrogen, their nominal concentrations in COMSOL are reduced by their molal concentrations in pure water (55.50621679636 $mol_O/kg_{water}$ and 111.0124335927 $mol_H/kg_{water}$, respectively). Even with this high accuracy, calculations of the redox potential (pe) in unbuffered solutions may not give reliable results and should be examined carefully. Equilibration with atmospheric $O_2$ stabilizes otherwise unbuffered solutions und should therefore be considered if applicable (Parkhurst and Appelo, 1999).

The COM-version of IPhreeqc (Charlton and Parkhurst, 2010) that is utilized in the presented coupling has a number of features that greatly simplify data handling:

- Reaction calculations can be entirely controlled from within Matlab by passing commands strings to the COM object.
- Changes in the reaction system due to transport of aqueous elements are considered by modifying the moles of elements in solution.
- No cumbersome writing/reading of files is necessary in order to pass results from the reaction module to the flow/transport module and vice versa. Data transfer via the Matlab workspace is processed entirely in memory.
- The status of the entire geochemical system, including all exchangers, surfaces, kinetics phases, mineral and gas phases, is automatically saved by the COM object in between calls.

As result of persistence of the geochemical properties in the COM object, the coupling procedure only needs to manage solution elements. This not only decreases programming effort and increases coupling efficiency but also eliminates the need for user-defined definitions of all possible exchange and surface species, as is found in earlier couplings involving PHREEQC (Prommer et al., 2003).

## 4 Verification example: Pesticide degradation

This application example reproduces the simulation of kinetic pesticide degradation in COMSOL's model library (COMSOL Multiphysics®, 2008b) using IPhreeqc instead of COMSOL's Reaction Engineer Lab® to simulate the reaction chain. According to COMSOL Multiphysics® (2008b), the simulation is inspired by but does not exactly duplicate the application example no. 7 of the software packages SWMS-2D (Šimůnek et al., 1994) and HYDRUS-2D (Šimůnek et al., 1999). Because of the identical treatment of unsaturated flow and solute transport, the application example can be regarded as a verification of the coupling procedure.

**Fig. 2. Simulation domain with finite element mesh for pesticide simulation. The source zone is indicated by the thick line at *y* = 0.**

The radially symmetric simulation domain with 4401 nodes and 26406 degrees of freedom is displayed in Fig. 2. The pesticide *Aldicarb* enters the dry soil via constant flux infiltration at the top boundary in the region $y$ = 0 m, 0 m ≤ $r$ ≤ 0.2 m. The soil is divided into two subdomains with different hydraulic properties, i.e., higher conductivity and lower saturated water content below $y$ = -0.4 m. The initial hydraulic head $h$ (m) of the simulation domain is given by the expression

$$h(y) = \begin{cases} -(y + 1.2\text{ m}), & y < -0.4\,m, \\ -(1.2y + 1.6\text{ m}), & y \geq -0.4\,m. \end{cases} \quad (5)$$

Transformations between Aldicarb and its breakdown products are governed by first-order rates according to Eqs. (6-11), where $n_i$ denotes moles of the chemical in the control volume (mol m$^{-3}$), $k_1 - k_5$ are reaction constants (s$^{-1}$), $c_i'$ denote total molal concentrations (mol $\text{kg}_{\text{water}}^{-1}$) and $w$ stands for the kilograms of water in the control volume (kg m$^{-3}$).

Aldicarb (a): $$\frac{\partial n_\text{a}}{\partial t} = -(k_1 c'_\text{a} + k_2 c'_\text{a})w; \quad (6)$$

Aldicarb Oxime (ao): $$\frac{\partial n_{\mathrm{ao}}}{\partial t} = k_1 c'_{\mathrm{a}} w; \quad (7)$$

Aldicarb Sulfoxide (asx): $$\frac{\partial n_{\mathrm{asx}}}{\partial t} = (k_2 c'_{\mathrm{a}} - k_3 c'_{\mathrm{asx}} - k_4 c'_{\mathrm{asx}}) w; \quad (8)$$

Aldicarb Sulfoxide Oxime (asxo): $$\frac{\partial n_{\mathrm{asxo}}}{\partial t} = k_3 c'_{\mathrm{asx}} w; \quad (9)$$

Aldicarb Sulfone (asn): $$\frac{\partial n_{\mathrm{asn}}}{\partial t} = -(k_4 c'_{\mathrm{asn}} + k_5 c'_{\mathrm{asn}}) w; \quad (10)$$

Aldicarb Sulfone Oxime (asno): $$\frac{\partial n_{\mathrm{asno}}}{\partial t} = k_5 c'_{\mathrm{asn}} w. \quad (11)$$

The reaction chain together with first-order rate constants is displayed schematically in Fig. 3.

**Fig. 3. Aldicarb reaction chain.**

To be consistent with the COMSOL example, it is necessary to prevent unwanted geochemical transformations. Therefore, Aldicarb and its daughter products were introduced into IPhreeqc as separate uncharged solution master species with no reactions apart from the transformations listed in Fig. 3. Further details of the breakdown process and the COMSOL solution are available in the COMSOL model library documentation (COMSOL Multiphysics®, 2008a). The coupling time step $\Delta t$ was set to 0.1 d.

**Fig. 4. Comparison of concentrations from the coupling procedure and COMSOL alone eight d after beginning of infiltration.**

In order to verify the coupling procedure, moisture content and concentrations were compared along the centre line (*r* = 0) with results from COMSOL alone (Fig. 4). Moisture contents from the coupled simulation (COMSOL+IPhreeqc) and the global implicit method in COMSOL (COMSOL) are visually indistinguishable. Small differences in chemical concentrations can be fully attributed to the splitting error, whose magnitude decreases linearly with $\Delta t$. If negative concentrations from the previous transport step are not summed to the concentrations after transport, as described in section 3, an obvious mass balance error with overestimation of all pesticide species is produced. Thus, the results prove the accuracy of the coupling procedure and particularly the successful suppression of significant mass balance errors that would result from the uncompensated adjustment of concentrations to positive values during reaction calculations.

## 5 Application example: Drip irrigation and fertigation

This example, reported by Hanson et al. (2006), simulates the fertigation of a tomato plantation using a subsoil micro-irrigation system with periodic input of water and fertilizer solution. The simulation of flow and transport was reproduced in COMSOL using the same domain properties and parameters as in Hanson et al. (2006), who applied HYDRUS-2D (Šimůnek et al., 1999). In contrast to Hanson et al. (2006), however, we implemented a detailed description of geochemical through the coupling to IPhreeqc. This included solution speciation with ion activity correction, kinetic redox transformations and cation exchange. In agreement with Hanson et al. (2006), root water uptake was simulated using the spatial root distribution model of Vrugt et al. (2001) in combination with the water stress response function of Feddes et al. (1978). The model was implemented through the Matlab function *root_uptake.m,* which is called from COMSOL at runtime (details on root water uptake are given by Šimůnek and Hopmans, 2009; Šimůnek et al., 1999).

**Fig. 5. Simulation domain with finite element mesh for drip irrigation simulation.**

The simulation domain with 2665 nodes and 23985 degrees of freedom is displayed in Fig. 5. It represents a 2D slice of the soil system with axial symmetry along the left boundary. Solutes and irrigation water enter the soil through the small half circle at $x$ = 0 m, $y$ = -0.2 m that represents the irrigation pipe with a diameter of 0.02 m. Irrigation imposes a constant flux for 1.15 d intermittent with no flow periods of 2.35 d. The fertilizer enters the domain for 0.575 d via a constant concentration boundary beginning 0.2875 d after start of irrigation periods. Details of the flow and solute transport properties are given by Hanson et al. (2006) and Gärdenäs et al. (2005) (simulation *SUBTAPE,* fertigation scenario *M50*).

Master species concentrations in the inflowing fertilizer solution were calculated by reacting 0.1449 mol $KH_2PO_4$, 0.0362 mol $NH_4NO_3$ [Amm$HNO_3$] and 0.0725 mol $(NH_2)_2CO$ [Urea] with 1 kg of pure water. In order to prevent instantaneous hydrolysis and nitrification, urea (Urea) and ammonia (Amm) were defined as separate solution master species in IPhreeqc. In addition, the fertilizer solution and the fertilizer-free irrigation water were equilibrated with atmospheric $CO_2$ ($10^{-3.5}$atm) and $O_2$ ($10^{-0.7}$ atm). The initial soil solution was assumed in equilibrium with atmospheric $O_2$ ($10^{-0.7}$ atm) and with $CO_2$ from root respiration at a partial pressure $10^{-1.5}$ atm. The latter value was chosen in agreement with the expected high actual evaporation (~1200 mm $yr^{-1}$) for an irrigated tomato plantation in California, USA (Hanson et al., 2006) according to Brook et al. (1983). Properties of inflowing and initial solutions are summarized in Table 1.

**Table 1**
**Geochemical solution properties. Master species concentrations in mol $kg_{water}^{-1}$, truncated to 2 digits.**

Equilibrium solution speciation was defined as given in the thermodynamic database *phreeqc.dat*, which is distributed with IPhreeqc. In order to suppress denitrification as in Hanson et al. (2006), the equilibrium constant for the reaction $2NO_3^- + 12H^+ + 10e^- \rightleftharpoons N_2 + 6H_2O$ was set to $10^{-1000}$. Kinetic hydrolysis of urea was simulated according to the reaction

$$\mathrm{Urea} + H_2O \rightarrow 2\mathrm{Amm} + CO_2, \tag{12}$$

with the first-order rate expression $r_{hyd}$ (mol $s^{-1}$ $m^{-3}$) (Hanson et al., 2006),

$$r_{\mathrm{hyd}} = k_{\mathrm{hyd}} c'_{\mathrm{Urea}} w, \tag{13}$$

where $k_{\mathrm{hyd}}$ is the reaction constant taken as -0.35 $d^{-1}$ and $c'_{\mathrm{Urea}}$ is the molal urea concentration. For the kinetic nitrification of ammonium to nitrate, we used the reaction formula

$$\mathrm{AmmH}^+ + 2O_2 = NO_3^- + 2H^+ + H_2O, \tag{14}$$

with the rate,

$$r_{\mathrm{nit}} = k_{\mathrm{nit}} c'_{\mathrm{Amm}}\, w\, \frac{c'_{\mathrm{O(0)}}}{c'^{0}_{\mathrm{O(0)}}}. \tag{15}$$

The reaction constant $k_{nit}$ was set to -0.2 $d^{-1}$. In Eq. (15), $c'_{\mathrm{Amm}}$ and $c'_{\mathrm{O(0)}}$ are the molal concentrations of ammonium and zero-valent oxygen, respectively, and $c'^{0}_{\mathrm{O(0)}}$ is the concentration of zero-valent oxygen in the initial solution ($5.11 \times 10^{-4}$ mol $kg_{water}^{-1}$). The last term in Eq. (15) was introduced as an additional factor to the rate expression of Hanson et al. (2006). Its purpose is to simulate free oxygen as a rate-limiting redox partner for the kinetic oxidation of ammonium to nitrate.

In contrast to Hanson et al. (2006), who used a simple linear isotherm for ammonium adsorption, we simulated adsorption of aqueous cations on negatively charged surfaces as a cation exchange process (Appelo and Postma, 2005). Besides potassium and ammonium, free protons ($H^+$) are included in the competition for the exchange sites in order to consider the pH dependence of cation exchange and to be consistent with the conceptualization of plant nutrient uptake via proton exchange (Hedrich and Schroeder, 1989). The cation exchange capacity was taken as 150 meq $l_{soil}^{-1}$, which is a reasonable value for loam (Yukselen and Kaya, 2006). Exchange reaction formulas and ion affinities with suggested values for proton exchange were those included in the database *phreeqc.dat.* The split-operator time step $\Delta t$ for the alternation between transport and reactions calculations was set to 0.01 d.

**Fig. 6. Normalized root distribution according to the Vrugt model (Vrugt et al., 2001) with parameters from Hanson et al. (2006).**

Fig. 6 displays the normalized root distribution function used to describe water and solute losses due to plant water uptake. As required by the Vrugt model (Vrugt et al., 2001), the normalized root distribution integrates to unity over the simulation domain. Clearly visible in Fig. 7 is the decrease of root density at depths $y < -0.2$ m, which is determined by the parameter $z^*$ in Hanson et al. (2006).

**Fig. 7. Moisture contents at 0 and 1.15 d, i.e., the beginning and end of the first irrigation period; white contours: lines of equal water contents.**

The successful re-simulation of moisture dynamics was verified by visually comparing moisture contents at the beginning and end of the first irrigation period with results presented in Gärdenäs et al. (2005) and Hanson et al. (2006) (To follow this comparison the reader is referred to the original references). The comparison reveals small discrepancies in the dry part of the domain and along the right no-flow boundary, which can be attributed to different domain discretizations and tolerance settings in the numerical methods.

**Fig. 8. Solution master species concentrations 3.88, 4.63, 5, 7 and 28 d after beginning of fertigation cycles.**

Molal concentrations of all solution master species, except for oxygen, hydrogen and carbon, are displayed in Fig. 8. In the model phosphorus (P) is not involved in any kinetic reactions or adsorption/desorption processes (since it does not adsorb to negatively charged sorption sites) and therefore can be used as a reference for conservative solute transport. By comparison to phosphorus and from concentrations of O(0) in Fig. 9 it is evident that the kinetic transformation of ammonium to nitrate is limited by the available O(0). Urea is clearly affected by hydrolysis with decreasing concentrations after fertigation periods and increasing concentrations of ammonia (Amm). Potassium (K) is strongly retarded compared to phosphorus, with equal inflowing and initial concentrations due to exchange with adsorbed protons and ammonia.

**Fig. 9. Moisture contents, pH and exchanger composition 3.88, 4.63, 5, 7 and 28 d after beginning of fertigation cycles.**

The exchanger composition, pH and molal concentrations of O(0) are presented in Fig. 9. The soil's low initial pH originates from respiratory $CO_2$. The decreasing pH behind the solute front can be attributed to (i) oxidation of ammonium and (ii) the replacement of protons from the surface exchange sites by ammonia and potassium. The latter can be interpreted as a proton "snow plough" (Barry et al., 1983).

Low pH values due to nitrification and proton exchange may result in significant dissolution of soil matrix minerals (e.g., calcite), which may act as pH buffers and release cations that compete for adsorption sites and thereby reduce the adsorption efficiency of fertilizer ions. Kinetic or equilibrium mineral reactions can be easily included in the simulation. However, this was not taken into account in the given example because of the unknown mineral composition of the substrate. Kinetic oxidation of ammonium to nitrate leads to a local depletion in O(0) concentrations that inhibits further nitrification according to Eq. (15). Due to the absence of other cations, the initial exchanger is entirely filled with $H^+$. This situation is unlikely to be valid in the field, but allows for more straightforward interpretation of this illustration. A more realistic exchanger initialization requires measured exchanger compositions or knowledge about the trace elements in the initial soil solution. Even though the exchanger has a slightly larger affinity for potassium, ammonium dominates the exchanger composition in the exterior of the solute ring that forms around the irrigation pipe. This is due to the elevated concentration of ammonium from urea hydrolysis and retardation of potassium, which shifts the concentration ratio towards ammonium. In addition, the low pH values in this region favour the formation of ammonium as opposed to non-adsorbing ammonia. Potassium is mainly adsorbed close to the irrigation pipe, where ammonium concentrations are low. The region at $x$ = 0.6 m, $y$ = 0 m remains extremely dry (cf. Fig. 7). Therefore, it is effectively inert towards changes in geochemical conditions (e.g., pH, O(0) content).

Results of the present simulation and those of Hanson et al. (2006) show roughly similar patterns for nitrate and urea. However, in our simulations nitrate concentrations at 7 and 28 d are considerably lower in the direct vicinity of the supply tube, where it shows the highest concentrations in Hanson et al. (2006). The lower concentration in our simulations is expected considering the irrigation/fertigation scheme where the fertilizer is flushed into the soil with pure water following its application.

## 6 Concluding remarks

The application example in section 4 verifies the coupling of unsaturated flow and multispecies solute transport in COMSOL with the geochemical modelling framework IPhreeqc. Minor differences to the global implicit solution are introduced through operator splitting and can be controlled by the magnitude of the splitting time step $\Delta t$. Furthermore, it was shown that the constraint of positive concentrations in IPhreeqc in combination with negative concentrations from COMSOL's solute transport scheme does not lead to significant mass balance errors.

Section 5 shows the enhanced geochemical capabilities resulting from the coupling between COMSOL and IPhreeqc in a complex simulation of unsaturated flow and solute transport. The successful replication of the moisture content distribution from Hanson et al. (2006) illustrates the capabilities of COMSOL's Earth Science Module to simulate unsaturated flow processes. Further, the implementation of pressure- and root distribution-dependent root-water uptake demonstrates the convenience of COMSOL to extend predefined vadose zone processes through user-defined Matlab functions.

Due to the capabilities of COMSOL to simulate a wide variety of environmental flow phenomena (e.g., two-phase flow, fracture flow, flow according to the Darcy, Brinkman or incompressible Navier-Stokes equations), the presented coupling procedure can be utilized as a general guide for linking flow and transport calculations in COMSOL to geochemical reactions in IPhreeqc.

## Acknowledgments

The authors wish to thank David Parkhurst and Tony Appelo for their assistance with the coupling procedure and the prompt implementation of the required features into PHREEQC.

This research was supported by Alcoa World Alumina Australia.

## References

Appelo, C.A.J., Postma, D., 2005. Geochemistry, Groundwater and Pollution, 2nd ed. Balkema, Leiden, Netherlands, 649 pp.

Barry, D.A., 1992. Modelling contaminant transport in the subsurface: Theory and computer programs, In: Ghadiri, H., Rose, C.W. (Eds.), Modelling Chemical Transport in Soil: Natural and Applied Contaminants. Lewis Publishers: Boca Raton, Florida, pp. 105-144.

Barry, D.A., Bajracharya, K., Crapper, M., Prommer, H., Cunningham, C.J., 2000. Comparison of split-operator methods for solving coupled chemical non-equilibrium reaction/groundwater transport models. Mathematics and Computers in Simulation 53(1-2) 113-127.

Barry, D.A., Miller, C.T., Culligan-Hensley, P.J., 1996. Temporal discretisation errors in non-iterative split-operator approaches to solving chemical reaction groundwater transport models. Journal of Contaminant Hydrology 22(1-2) 1-17.

Barry, D.A., Miller, C.T., Culligan, P.J., Bajracharya, K., 1997. Analysis of split operator methods for nonlinear and multispecies groundwater chemical transport models. Mathematics and Computers in Simulation 43(3-6) 331-341.

Barry, D.A., Starr, J.L., Parlange, J.Y., Braddock, R.D., 1983. Numerical analysis of the snow-plow effect. Soil Science Society of America Journal 47(5) 862-868.

Bear, J., 1972. Dynamics of Fluids in Porous Media. Elsevier Scientific Publishing Co, New York, 764 pp.

Bear, J., 2007. Hydraulics of Groundwater, Reprint ed. Dover Publications, Mineola, NY, 569 pp.

Bear, J., Bachmat, Y., 1998. Introduction to Modeling of Transport Phenomena in Porous Media, Reprinted ed. Kluwer, Dordrecht, 553 pp.

Brook, G.A., Folkoff, M.E., Box, E.O., 1983. A world model of soil carbon-dioxide. Earth Surface Processes and Landforms 8(1) 79-88.

Brooks, R.H., Corey, A.T., 1964. Hydraulic properties of porous media, Hydrological Paper. Civil Engineering Department, Colorado State University: Fort Collins, Colorado.

Brussaard, L., Pulleman, M.M., Ouédraogo, É., Mando, A., Six, J., 2007. Soil fauna and soil function in the fabric of the food web. Pedobiologia 50(6) 447-462.

Charlton, S.R., Parkhurst, D.L., 2010. Modules based on the geochemical model PHREEQC for use in scripting languages and reactive-transport calculations. Environmental Modelling & Software, under review.

COMSOL Multiphysics®, 2008a. Pesticide transport and reaction in soil, Earth Science Module Model Library.

COMSOL Multiphysics®, 2008b. Variably saturated flow and transport: Sorbing solute, Earth Science Module Model Library.

COMSOL Multiphysics®, 2010. http://www.comsol.com/, last accessed: 22.06.2010.

Corey, A.T., Auvermann, B.W., 2003. Transport by advection and diffusion revisited. Vadose Zone Journal 2(4) 655-663.

Donea, J., Huerta, A., 2004. Finite Element Methods for Flow Problems. Wiley, England, 350 pp.

Dzombak, D.A., Morel, F.M.M., 1990. Surface Complexation Modeling : Hydrous Ferric Oxide. Wiley, New York, 393 pp.

Feddes, R.A., Kowalik, P.J., Zaradny, H., 1978. Simulation of Field Water Use and Crop Yield. Pudoc, Wageningen.

Freedman, V., Ibaraki, M., 2002. Effects of chemical reactions on density-dependent fluid flow: on the numerical formulation and the development of instabilities. Advances in Water Resources 25(4) 439-453.

Gärdenäs, A.I., Hopmans, J.W., Hanson, B.R., Šimůnek, J., 2005. Two-dimensional modeling of nitrate leaching for various fertigation scenarios under micro-irrigation. Agricultural Water Management 74(3) 219-242.

Gustafsson, J.P., 2010. Visual MINTEQ version 3.0, http://www.lwr.kth.se/English/OurSoftware/vminteq/, last accessed: 22.06.2010.

Hanson, B.R., Šimůnek, J., Hopmans, J.W., 2006. Evaluation of urea-ammonium-nitrate fertigation with drip irrigation using numerical modeling. Agricultural Water Management 86(1-2) 102-113.

Harbaugh, A.W., Banta, E.R., Hill, M.C., McDonald, M.G., 2000. MODFLOW-2000, the U.S. Geological Survey modular ground-water model: User guide to modularization concepts and the ground-water flow process. U.S. Geological Survey.

Hedrich, R., Schroeder, J.I., 1989. The physiology of ion channels and electrogenic pumps in higher-plants. Annual Review of Plant Physiology and Plant Molecular Biology 40 539-569.

Hiemstra, T., van Riemsdijk, W.H., Bolt, G.H., 1989. Multisite proton adsorption modeling at the solid-solution interface of (hydr)oxides - A new approach. 1. Model description and evaluation of intrinsic reaction constants. Journal of Colloid and Interface Science 133(1) 91-104.

Huyakorn, P.S., Pinder, G.F., 1983. Computational Methods in Subsurface Flow. Academic Press, London, UK, 473 pp.

Jacques, D., Šimůnek, J., 2010. Notes on HP1 - a software package for simulating variably-saturated water flow, heat transport, solute transport and biogeochemistry in porous media Waste and Disposal, SCK•CEN: Mol, Belgium.

Jacques, D., Šimůnek, J., Mallants, D., van Genuchten, M.T., 2006. Operator-splitting errors in coupled reactive transport codes for transient variably saturated flow and contaminant transport in layered soil profiles. Journal of Contaminant Hydrology 88(3-4) 197-218.

Jacques, D., Šimůnek, J., Mallants, D., van Genuchten, M.T., 2008. Modeling coupled hydrologic and chemical processes: Long-term uranium transport following phosphorus fertilization. Vadose Zone Journal 7(2) 698-711.

Langmuir, D., 1997. Aqueous Environmental Geochemistry. Prentice Hall, Upper Saddle River, 600 pp.

Letey, J., Kemper, W.D., Noonan, L., 1969. Effect of osmotic pressure gradients on water movement in unsaturated soil. Soil Science Society of America Proceedings 33(1) 15-18.

Mao, X., Prommer, H., Barry, D.A., Langevin, C.D., Panteleit, B., Li, L., 2006. Three-dimensional model for multi-component reactive transport with variable density groundwater flow. Environmental Modelling & Software 21(5) 615-628.

Matlab®, 2010. The MathWorks, http://www.mathworks.com/, last accessed: 22.06.2010.

Mayer, K.U., Frind, E.O., Blowes, D.W., 2002. Multicomponent reactive transport modeling in variably saturated porous media using a generalized formulation for kinetically controlled reactions. Water Resources Research 38(9) 131-1321.

Meeussen, J.C.L., 2003. ORCHESTRA: An object-oriented framework for implementing chemical equilibrium models. Environmental Science & Technology 37(6) 1175-1182.

Miller, C.T., Christakos, G., Imhoff, P.T., McBride, J.F., Pedit, J.A., Trangenstein, J.A., 1998. Multiphase flow and transport modeling in heterogeneous porous media: Challenges and approaches. Advances in Water Resources 21(2) 77-120.

Millington, R.J., Quirk, J.P., 1961. Permeability of porous solids. Transactions of the Faraday Society 57 1200-1207.

Parkhurst, D.L., 2010. Personal Communication.

Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey: Denver, Colorado.

Parkhurst, D.L., Kipp, K.L., Engesgaard, P., Charlton, S.R., 2004. PHAST - A Program for simulating ground-water flow, solute transport, and multicomponent geochemical reactions. U.S. Geological Survey: Denver, Colorado.

Perrochet, P., Berod, D., 1993. Stability of the standard Crank-Nicolson-Galerkin scheme applied to the diffusion-convection equation - Some new insights. Water Resources Research 29(9) 3291-3297.

Prommer, H., Barry, D.A., Zheng, C., 2003. MODFLOW/MT3DMS-based reactive multicomponent transport modeling. Ground Water 41(2) 247-257.

Prommer, H., Davis, G.B., Barry, D.A., 1999. PHT3D - A three-dimensional biogeochemical transport model for modelling natural and enhanced remediation, In: Johnston, C.D. (Ed.), Contaminated Site Remediation: Challenges Posed by Urban and Industrial Contaminants. Centre for Groundwater Studies: Fremantle, Western Australia, pp. 351-358.

Saaltink, M.W., Batlle, F., Ayora, C., Carrera, J., Olivella, S., 2004. RETRASO, a code for modeling reactive transport in saturated and unsaturated porous media. Geologica Acta 2(3) 235-251.

Šimůnek, J., Bradford, S.A., 2008. Vadose zone modeling: Introduction and importance. Vadose Zone Journal 7(2) 581-586.

Šimůnek, J., Hopmans, J.W., 2009. Modeling compensated root water and nutrient uptake. Ecological Modelling 220(4) 505-521.

Šimůnek, J., Jacques, D., van Genuchten, M.T., Mallants, D., 2006. Multicomponent geochemical transport modeling using HYDRUS-1D and HP1. Journal of the American Water Resources Association 42(6) 1537-1547.

Šimůnek, J., Šejna, M., Saito, H., Sakai, M., van Genuchten, M.T., 2009. The HYDRUS-1D software package for simulating the movement of water, heat, and multiple solutes in variably saturated media, Version 4.0. Department of Environmental Sciences, University of California Riverside: Riverside, California.

Šimůnek, J., Šejna, M., van Genuchten, M.T., 1999. The HYDRUS-2D software package for simulating the two-dimensional movement of water, heat, and multiple solutes in variably-saturated media, Version 2.0. Department of Environmental Sciences, University of California Riverside: Riverside, California.

Šimůnek, J., Vogel, T., van Genuchten, M.T., 1994. The SWMS-2D code for simulating water flow and solute transport in two-dimensional variably saturated media, Version 1.21. U.S. Salinity Laboratory: Riverside, CA.

Steefel, C.I., MacQuarrie, K.T.B., 1996. Approaches to modeling of reactive transport in porous media, In: Lichtner, P.C., Steefel, C.I., Oelkers, E.H. (Eds.), Reactive Transport in Porous Media. Reviews in Mineralogy, 34. Mineralogical Society of America: Washington DC, pp. 82-129.

Valocchi, A.J., Malmstead, M., 1992. Accuracy of operator splitting for advection-dispersion-reaction problems. Water Resources Research 28(5) 1471-1476.

van der Lee, J., 1998. Thermodynamic and mathematical concepts of CHESS. Ecole des Mines de Paris: Fontainebleau, France.

van Genuchten, M.T., 1980. Closed-form equation for predicting the hydraulic conductivity of unsaturated soils. Soil Science Society of America Journal 44(5) 892-898.

Voss, C.I., Provost, A.M., 2008. SUTRA: A model for saturated-unsaturated, variable-density ground-water flow with solute or energy transport. U.S. Geological Survey: Reston, Virginia.

Vrugt, J.A., Hopmans, J.W., Šimůnek, J., 2001. Calibration of a two-dimensional root water uptake model. Soil Science Society of America Journal 65(4) 1027-1037.

Wissmeier, L., Barry, D.A., 2010. Implementation of variably saturated flow into PHREEQC for the simulation of biogeochemical reactions in the vadose zone. Environmental Modelling & Software 25(4) 526-538.

Wissmeier, L., Brovelli, A., Robinson, C., Stagnitti, F., Barry, D.A., 2009. Pollutant fate and transport in the subsurface, Modelling of Pollutants in Complex Environmental Systems. ILM Publications, pp. 99-143.

Yeh, G.T., Tripathi, V.S., 1989. A critical evaluation of recent developments in hydrogeochemical transport models of reactive multi-chemical components. Water Resources Research 25(1) 93-108.

Yukselen, Y., Kaya, A., 2006. Prediction of cation exchange capacity from soil index properties. Clay Minerals 41(4) 827-837.

## Table

Table 1

Geochemical solution properties. Master species concentrations in mol(kg water)$^{-1}$, truncated to 2 digits.

| | Fertilizer solution | Irrigation water | Initial soil solution |
|---|---|---|---|
| pH | 3.844 | 5.659 | 4.660 |
| pe | 16.78 | 14.96 | 15.96 |
| O | 56.12 | 55.51 | 55.51 |
| H | 111.34 | 111.01 | 111.02 |
| P | 0.15 | 0.00 | 0.00 |
| K | 0.15 | 0.00 | 0.00 |
| Amm | $3.62 \times 10^{-2}$ | 0.00 | 0.00 |
| Urea | $7.25 \times 10^{-2}$ | 0.00 | 0.00 |
| N | $3.62 \times 10^{-2}$ | 0.00 | 0.00 |
| C | $1.04 \times 10^{-5}$ | $1.30 \times 10^{-5}$ | $1.10 \times 10^{-3}$ |

## Figure Captions

Fig. 1. Program flow and structure.

Fig. 2. Simulation domain with finite element mesh for pesticide simulation. The source zone is indicated by the thick line at $y = 0$.

Fig. 3. Aldicarb reaction chain.

Fig. 4. Comparison of concentrations from the coupling procedure and COMSOL alone eight d after beginning of infiltration.

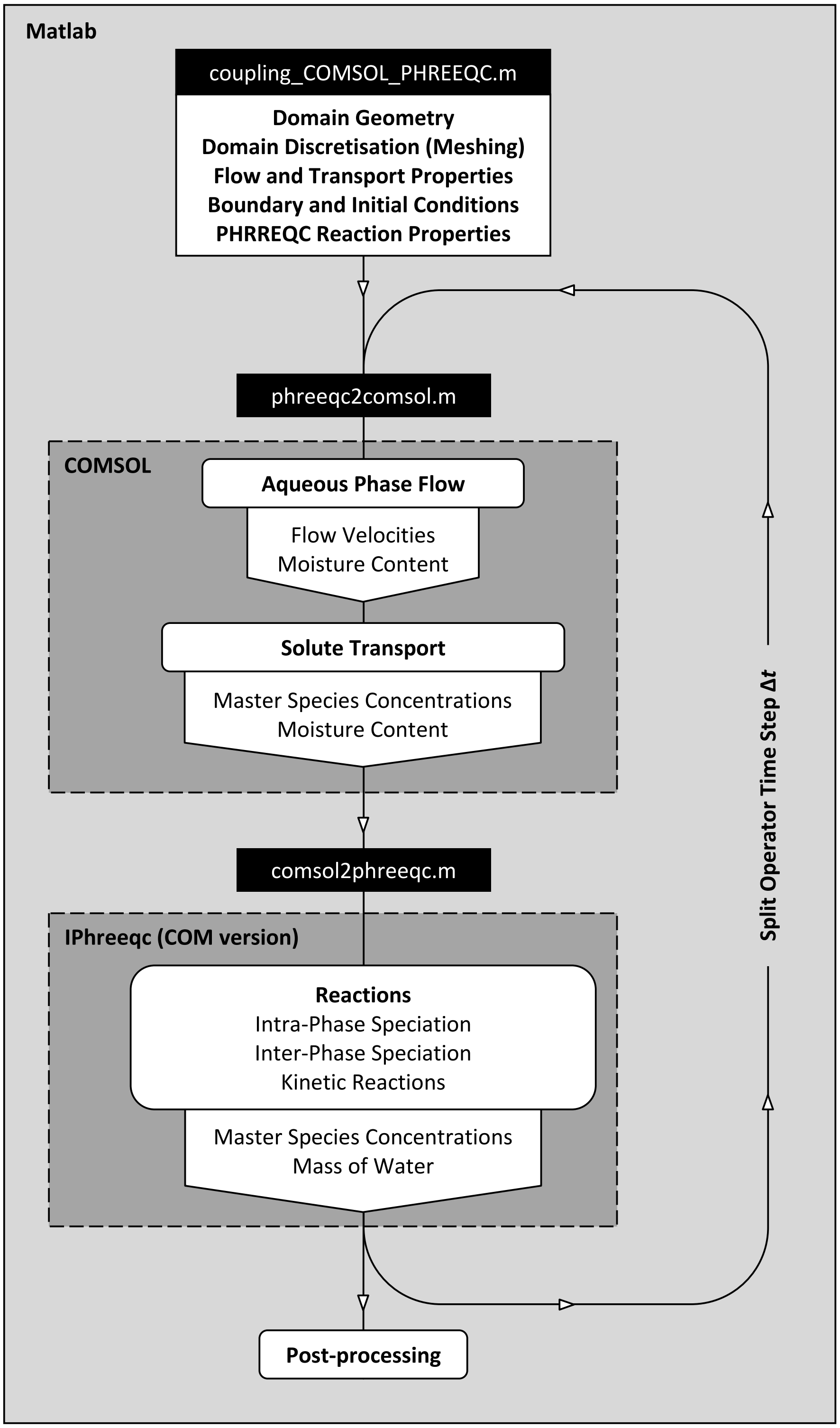
Fig. 5. Simulation domain with finite element mesh for drip irrigation simulation.

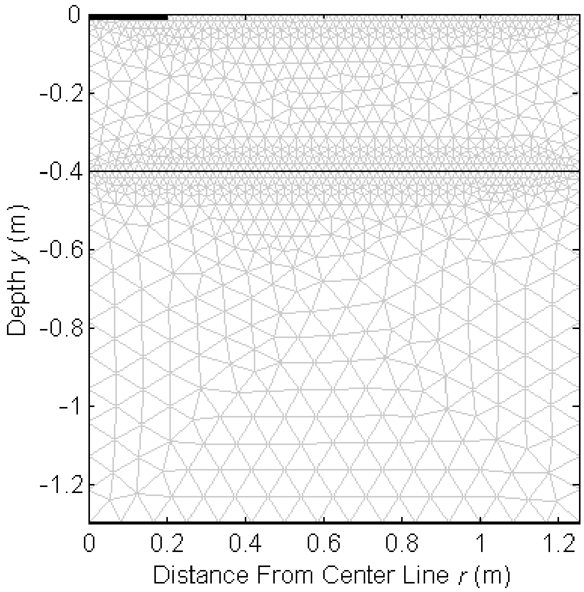
Fig. 6. Normalized root distribution according to the Vrugt model (Vrugt et al., 2001) with parameters from Hanson et al. (2006).

Fig. 7. Moisture contents at 0 and 1.15 d, i.e., the beginning and end of the first irrigation period; white contours: lines of equal water contents.

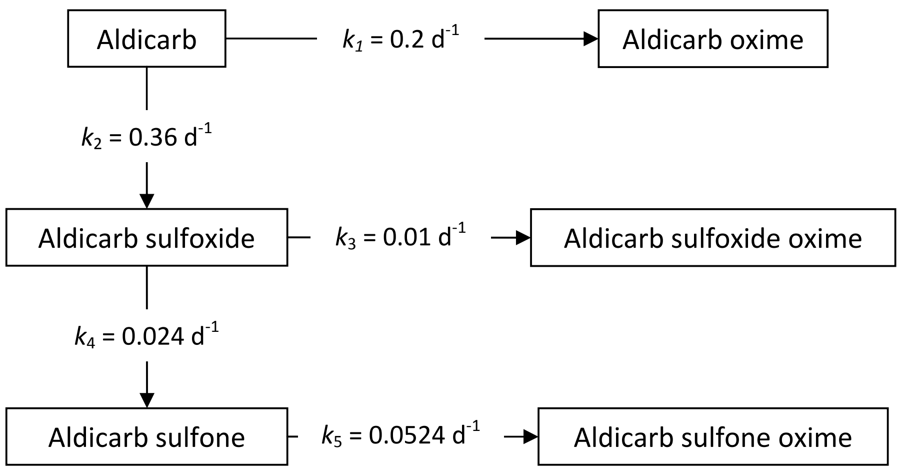
Fig. 8. Solution master species concentrations 3.88, 4.63, 5, 7 and 28 d after beginning of fertigation cycles.

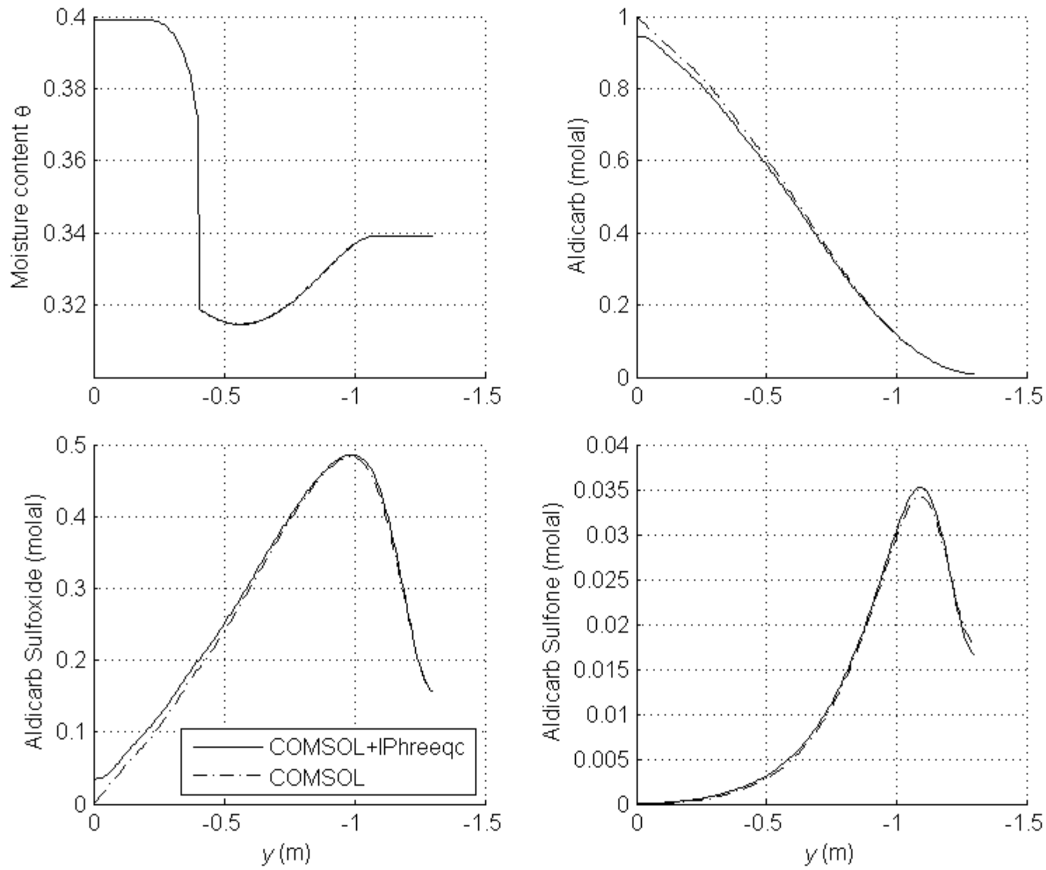
Fig. 9. Moisture contents, pH and exchanger composition 3.88, 4.63, 5, 7 and 28 d after beginning of fertigation cycles.


Matlab
coupling_COMSOL_PHREEQC.m
Domain Geometry
Domain Discretisation (Meshing)
Flow and Transport Properties
Boundary and Initial Conditions
PHRREQC Reaction Properties
phreeqc2comsol.m
COMSOL
Aqueous Phase Flow
Flow Velocities
Moisture Content
Solute Transport
Master Species Concentrations
Moisture Content
comsol2phreeqc.m
IPhreeqc (COM version)
Reactions
Intra-Phase Speciation
Inter-Phase Speciation
Kinetic Reactions
Master Species Concentrations
Mass of Water
Post-processing
Split Operator Time Step Δt

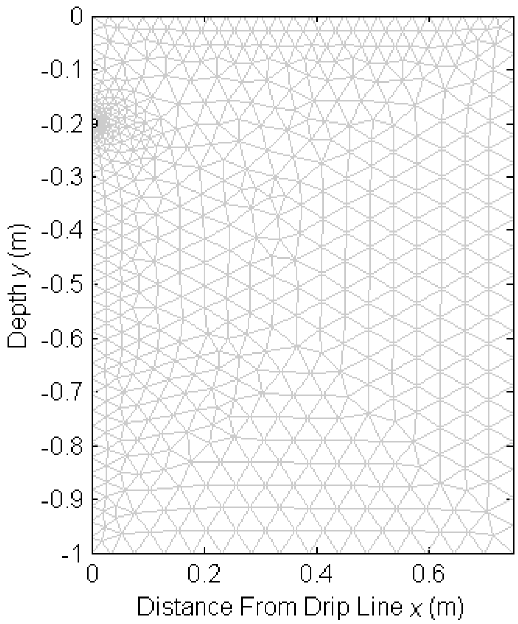


0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
Depth y (m)
0
0.2
0.4
0.6
0.8
1
1.2
Distance From Center Line r (m)

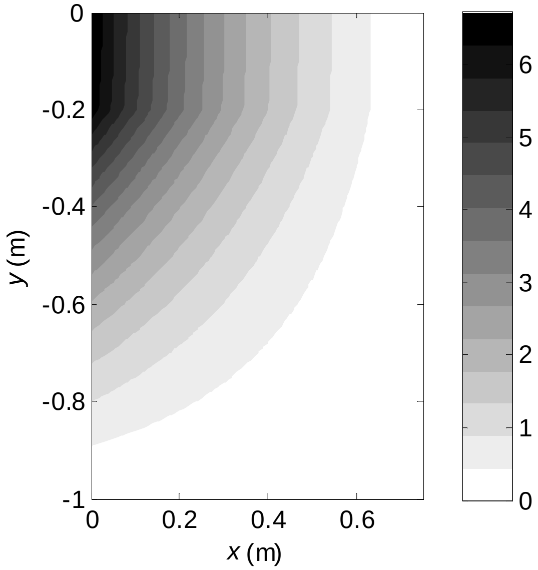

Aldicarb
$k_1$ = 0.2 d$^{-1}$
Aldicarb oxime
$k_2$ = 0.36 d$^{-1}$
Aldicarb sulfoxide
$k_3$ = 0.01 d$^{-1}$
Aldicarb sulfoxide oxime
$k_4$ = 0.024 d$^{-1}$
Aldicarb sulfone
$k_5$ = 0.0524 d$^{-1}$
Aldicarb sulfone oxime



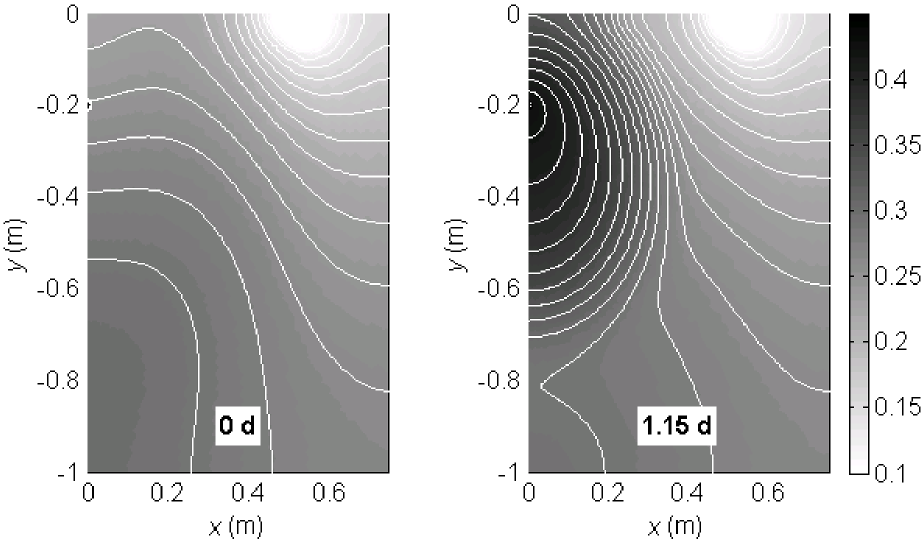
Moisture content θ
Aldicarb (molal)
Aldicarb Sulfoxide (molal)
Aldicarb Sulfone (molal)
COMSOL+IPhreeqc
COMSOL
y (m)
y (m)

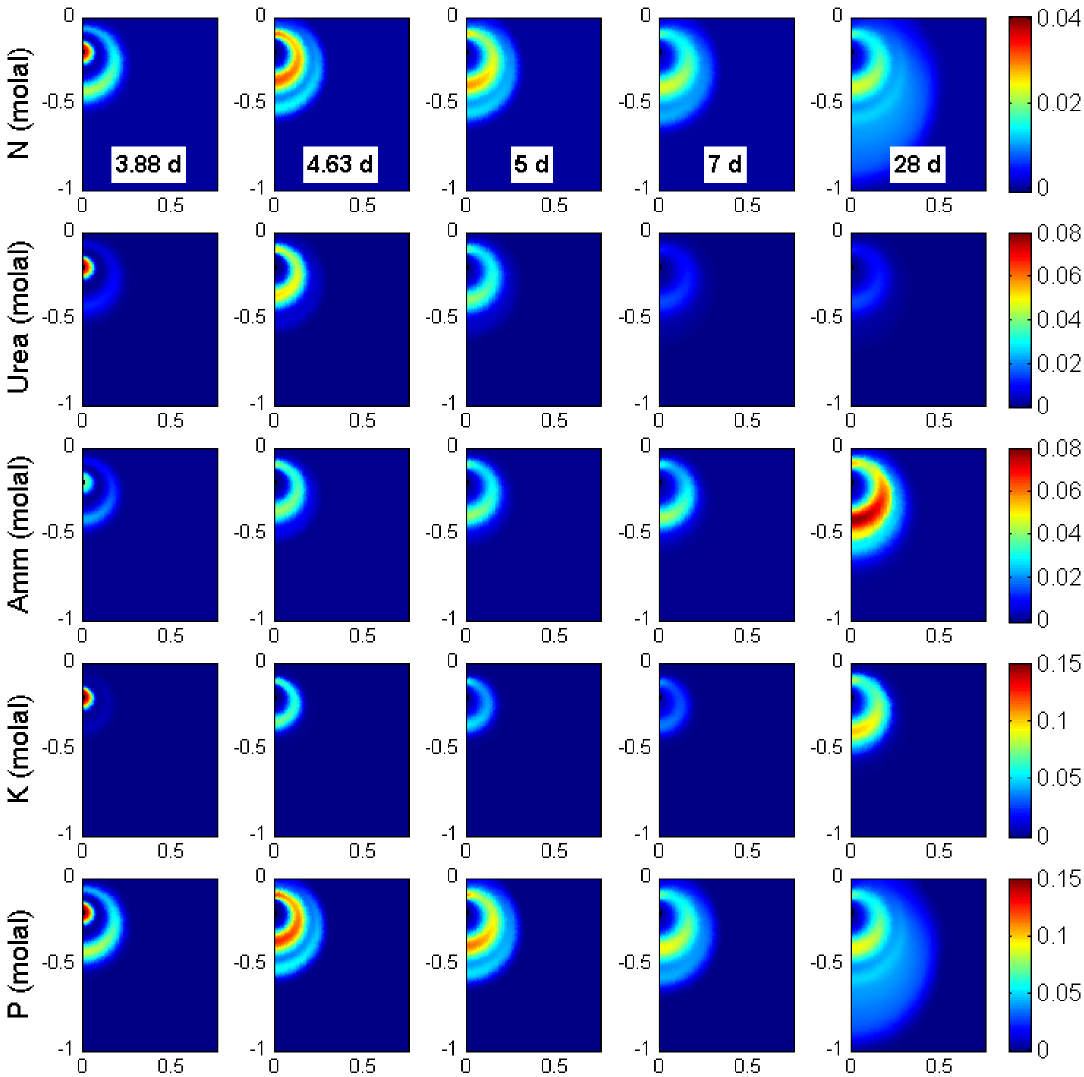


0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
Depth y (m)
0
0.2
0.4
0.6
Distance From Drip Line x (m)

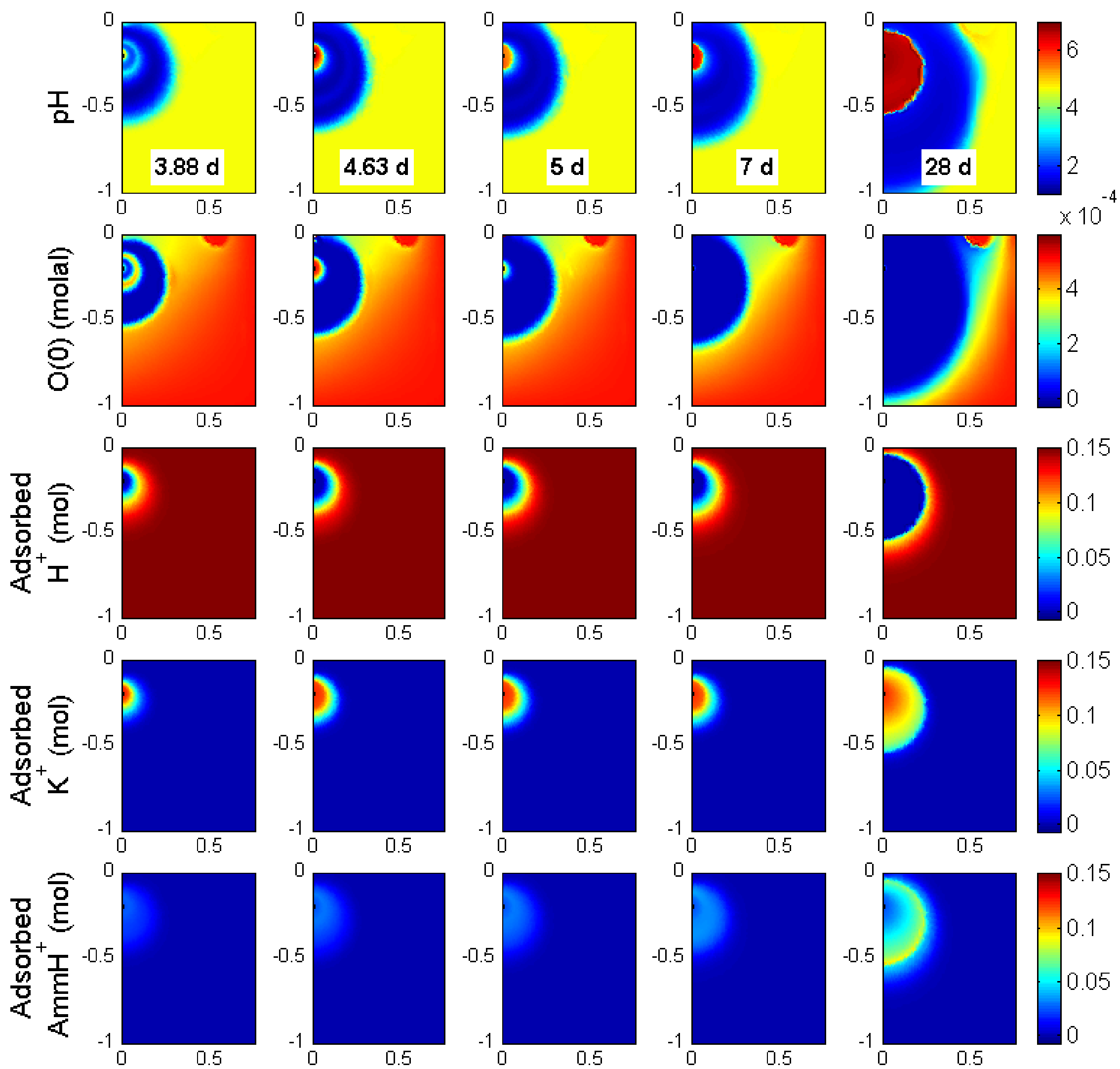


0
-0.2
-0.4
-0.6
-0.8
-1
y (m)
0
0.2
0.4
0.6
x (m)
6
5
4
3
2
1
0


0
-0.2
-0.4
-0.6
-0.8
-1
y (m)
0
0.2
0.4
0.6
x (m)
0 d
1.15 d
0.4
0.35
0.3
0.25
0.2
0.15
0.1



N (molal)
Urea (molal)
Amm (molal)
K (molal)
P (molal)
3.88 d
4.63 d
5 d
7 d
28 d
0.04
0.02
0.08
0.06
0.15
0.1
0.05
0
-0.5
-1
0.5



pH
O(0) (molal)
Adsorbed H+ (mol)
Adsorbed K+ (mol)
Adsorbed AmmH+ (mol)
3.88 d
4.63 d
5 d
7 d
28 d
x 10-4