SMART

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Computational model for the simulation of Partially saturated flow and transport:

Assessment of existing software for the numerical solution of multi-species reactive transport problems in partially saturated water flow

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1 Abstract

HYDRUS-HP1, PFLOTRAN and TOUGHREACT have been assessed for the solution of multi-species reactive transport problems in partially saturated media mainly for the purpose of supporting the design and planning of artificial recharge systems. In the current assessment, a calcite dissolution problem with all the reactions assumed to be at equilibrium has been considered. The solutions obtained have been compared showing a good agreement between the three software packages. Among the tested software PFLOTRAN seems to be the most attractive mainly due to its parallel processing capability and robustness, which becomes an essential feature for potentially large scale multiple variable problems.

2 Objective

The main objective of this work is to test and validate available software for the solution of multi-species reactive transport problems in variably saturated media for application to the design and planning of the aquifer artificial recharge with waters of varying qualities. Particular interest is given to the modelling capabilities, robustness, and usability of the software under scrutiny.

3 Governing equations

In the following the governing equations that describe mathematically the water flow and the reactive transport in variably saturated conditions are reported.

3.1 Flow equation

An approximate description of water flow in and unsaturated soil can be obtained neglecting phase change effects and assuming that the gas phase acts as a "passive bystander" with negligible pressure gradients. Under these assumptions the following equation for liquid phase flow is obtained (Bear 1987):

$$\frac{\partial \varphi \rho s}{\partial t} + \frac{\partial \rho q_i}{\partial x_i} = Q_w \qquad q_i = -\frac{kk_r}{\mu}\frac{\partial}{\partial x_i}\left(p - \rho gz\right) \tag{1}$$

Where φ is the porosity, s is liquid saturation, k_r is the relative permeability, k is the intrinsic permeability and Q_W is the mass source/sink. Neglecting variations in liquid phase density and viscosity, as is appropriate for (nearly) isothermal conditions, Eq. (1) simplifies to Richards' equation (1931):

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x_i}\left[K\left(K_{ij}^A \frac{\partial h}{\partial x_j} + K_{iz}^A \right) \right] - S_W \tag{2}$$

Where $h = p/\rho g$ is the water pressure head, $\vartheta = s\varphi$ is the volumetric moisture content, $K = kk_r \rho g/\mu$ is the hydraulic conductivity, K_{ij}^A is the, dimensionless, anisotropy tensor and $S_W = Q_W/\rho$ is the volumetric source/sink.

3.2 Multi-species reactive transport

A mathematical description of a multi-species reactive transport for the unsaturated zone of the aquifer is given by:

$$\frac{\partial \vartheta c_n}{\partial t} = \frac{\partial}{\partial x_i}\left(\vartheta D_{ij}^S \frac{\partial c_n}{\partial x_j} \right) - \frac{1}{\varphi}\frac{\partial q_i c_n}{\partial x_i} + R_n\left(c_l\right) \quad \text{with} \quad n = 1, N_{sp} \tag{3}$$

where c_n is the concentration of one of the N_{sp} species considered in the system, D_{ij}^S is the dispersivity tensor, φ is the porosity of the medium, q_i the water flux, $R_n\left(c_l\right)$ is the reaction term

that in general depends from all the species ($l = 1, N_{sp}$). Equation (3) can be rewritten in a more concise form dividing the transport operator from the reaction operator

$$\frac{\partial \vartheta c_n}{\partial t} = L^{AD}\left(c_n\right) + R_n\left(c_l\right)$$ (4)

Where

$$L^{AD}\left(\ \right) = \frac{\partial}{\partial x_i}\left(\vartheta D_{ij}^S \frac{\partial(\ )}{\partial x_j}\right) - \frac{1}{\varphi}\frac{\partial q_i(\ )}{\partial x_i}$$ (5)

The operator L^{AD} takes account only of the advective-dispersive transport while R_n expresses the interaction between the species considered, and its model is strictly related to the nature of the chemical reactions. In general this is a non-linear term.

4   Numerical approaches

The equations presented above need to be discretised in order to allow a numerical solution. The most common (and commonly accepted) numerical methods adopted for the solution of equations (1) (2) and (3) are the finite element and the finite volumes approaches. Finite Elements usually tends to provide more accurate results while the second is more robust and has the great advantage of a ensuring mass conservation. A general analysis of the numerical schemes used for the solution of partial differential equations is beyond the scope of this deliverable. However, references are provided for those interested in the implementation of the numerical techniques.

For a better understanding on how the chemical system is implemented within the software that will be considered later, it is worth recalling some of the numerical approaches to reactive transport and to the coupling of the reaction and transport terms (Eq. 3 and 4)

The reaction term affects the local concentrations which in turn determine the fluxes of aqueous species. In the same way, the magnitude of the fluxes can affect the reaction rates. An accurate solution of the overall problem, therefore, requires that the terms be coupled to some level. Several methods have been proposed to solve the coupled set of equations. The most straightforward way conceptually, but the most demanding from a computational efficiency point of view, is to simultaneously solve the governing equations, including both reaction and transport terms. This approach is referred to as a one-step or global implicit method.

Alternatively, it is possible to use operator splitting techniques to decouple the reaction and transport calculations. The classic time-splitting approach to solving the coupled set of equations as the sequential non-iterative approach (SNIA) consists of solving the reaction and transport equations within a single time step in sequence, with no iteration between flow and chemistry. Another available method is the sequential iteration approach or SIA where the reaction and transport are solved separately but iteration between the two calculations is carried out until a converged solution is attained. For a full review and description of the coupling methods see Steefel and MacQuarrie (1996).

Of particular interest for the remainder of this work is the case in which the chemical processes take place so fast that they can be considered practically instantaneous when compared to the transport

phenomena speed, i.e. we assume that the reaction is in equilibrium. The fact that equilibrium can be assumed for a part or all the reactions considered in the chemical system, determines the type of formulation chosen to solve the problem (Steefel and MacQuarrie 1996). When all of the species can be considered to be at equilibrium, the chemical problem can be completely decoupled from the transport, and local speciation driven by algebraic expressions based on mass action expressions are considered to take account of the chemistry. In this case it is common practice to divide the species in 'primary species' (or 'components') and 'secondary species' (or 'non-components'), with the number of secondary species equal to the number of equilibrium reactions. In order to reduce the number of equations that need to be discretised globally, only the transport for the total concentration of the 'primary species' is solved, which by definition is reaction free (Steefel and MacQuarrie 1996). Note that the total concentration of a primary species is the stoichiometric sum of the concentrations of the species that contains the primary species

$$\Psi_j = c_j + \sum_i^{Ns} v_{ij} c_i \tag{5}$$

Where Ψ_j is the total concentration, c_j is the primary species, c_i are secondary species, v_{ij} are the stoichiometric coefficients. In this approach the extra equations needed to close the system and to compute the individual concentrations of each species are given by the mass action laws of the equilibrium reactions. These expressions relate the secondary and the primary species with the total concentrations, and even though these algebraic equations are local, they are usually non-linear. The transport equation for the total concentration is given by:

$$\frac{\partial \vartheta \Psi_j}{\partial t} = L^{AD}\left(\Psi_j\right) + R_j \tag{6}$$

Where R_J includes possible sorption and dissolution/precipitation terms. This approach cannot be used when the boundary conditions (BCs) for the total concentration are not known.

5 Software capabilities and feature

Three software packages have been selected and will be assessed for simulations of multi-species reactive transport problems in porous medium under variably saturated water flow conditions: HYSDRUS-HP1, TOUGHREACT, and PFLOTRAN. An overview of each software package is detailed as follows. Their suitability to solve the problem is analysed first, then their method of handling the input/output data and their usability is also outlined.

5.1 HYDRUS-HP1

HYDRUS has been developed for agriculture applications, and it is designed to model a series of irrigation and fertigation problems with a very intuitive graphical user interface (GUI). It can solve variably saturated water flow and reactive transport of multiple solutes in multilayered soil. Fractured porous medium can also be modelled using the dual porosity approach. If required, the heat transport equation is added to the solution for those problems in which the temperature distribution is important (Šimůnek et al. 2006).

The air phase is assumed to be stationary and at atmospheric pressure, and its effect on the water flow is neglected. The water is considered to be incompressible. The pressure distribution and the resulting flow are then studied solving a simplified version of the Richards' equation (Eq. 2). A

selection of saturation and permeability functions is available (e.g. Van Genutchen, Books-Corey, etc). The porous matrix is assumed to be rigid.

The solutes are transported by advection, diffusion and dispersion, and the reaction between chemical species, the sorption and the dissolution/precipitation phenomena are modelled using zero and first-order functions with coefficients that must be determined empirically via calibration with experiments.

For HYDRUS 2D/3D, the one explained above is the only available approach to include chemical reactions. For one-dimensional problems, a version of the software called HP1, see Jacques and Šimůnek (2005), is also available, which couples the solution of the variably saturated flow and solute transport with the PHREEQC chemical database (Parkhurst and Appelo 1999). HP1 uses HYDRUS 1D to solve the variably saturated flow, and implements a total concentration formulation as the one described in section 3 to model multi-species reactive transport problems. The local chemical speciations are performed locally calling PHREEQC. Only the SNIA approach is available to couple the transport and reaction term of Eq. (6).

The finite element method is adopted for the discretisation of the partial differential equations with the option of switching on the UPWIND or an artificial dispersivity scheme to handle the instabilities rising from the advection terms (Jacques and Šimůnek 2005).

The software GUI includes pre- and post- processing capabilities. The mesh can be generated and displayed internally. The problem definition parameters (e.g. hydrogeological parameters, material constitutive relations, etc), and numerical simulation parameters are passed to HYDRUS and HP1 via this GUI.

The simulation output can also be analysed using the GUI that allows the creation and visualisation of data profiles and contour plots without recurring to the help of external packages.

5.2   TOUGHREACT

TOUGHREACT can be applied to a large variety of reactive fluid and geochemical transport systems: contaminant of transport with linear adsorption and decay, natural groundwater quality evolution under ambient conditions, assessment of nuclear waste disposal sites, CO_2 disposal in deep formation, etc., see Xu et al. (2004).

This package differs from standard variably saturated water flow and transport solvers for the following three features: (a) the gas phase is active for multiphase fluid flow, mass transport and chemical reactions, (b) not only porous medium is considered, but also reactive fluid and transport in fractured rocks, (c) the effect of heat can be considered, including heat-driven fluid flow, and temperature-dependent thermo-physical and geochemical properties (such as fluid density and viscosity, and thermodynamic and kinetic data). In addition to the flow equation, the energy conservation equation is also solved for the temperature. Several options for the equation of state are available within the package to relate the thermodynamic variables (pressure, density, temperature). Temporal changes in porosity and permeability due to mineral dissolution and precipitation processes can also be modelled.

Transport of aqueous and gaseous species by advection and molecular diffusion is considered in both liquid and gas phases. The software uses an alternative approach to the standard Fickian dispersion model. In fact, the software's authors do not consider this type of approach realistic for the large scale problems they intend to solve (e.g. unrealistic large level of mixing and dilution). Instead, dispersion is modelled through appropriate spatial resolution on multiple scales, using the

multiple continua (or multi-region) models to describe interactions between fluid regions with different velocities.

The transport equations are written in terms of total concentration of primary species, and all the interaction between aqueous species, and cation exchange phenomena, are considered under the local equilibrium assumption (see Eq. 5 and 6). Mineral dissolution and precipitation can proceed either to local equilibrium or kinetic conditions. The software has an internal chemical database that can be modified to add additional chemical system to those already implemented (e.g. definition of new primary and secondary species, etc.)

Although the software can handle multiphase flow problems, a module for the solution of a single phase in partially saturated porous medium is available (EOS9), which solves Eq. 1. This module retains all the features of the multiphase version of the software (variability of density and viscosity with temperature, variable porosity, etc.). In addition to all the standard saturation and permeability functions (e.g. Van Genutchen, Books-Corey, etc.) that are already implemented, the software gives the possibility to implement a customised set of function in a very simple way (Pruess et al. 1999).

The control volume numerical method is adopted for the discretisation of the partial differential equations with the possibility of using a classical UPWIND scheme to deal with the advection terms. At the moment only a sequential version of the software is available (Xu et al. 2004).

The input parameters (permeability, etc.) are provided to TOUGHREACT by means of several ASCII data files, with up to 80 characters per record. The data is organised into blocks, each being identified and introduced in the input files by a unique self-explanatory key-word.

The computational mesh (i.e. the spatially-discretised geometry), which is required for each simulation, can either be generated internally via TOUGHREACT, using MeshMaker, or can be provided using external software. A large number of external mesh generation software packages are available for this purpose. If the internal MeshMaker is used, an additional input block containing the geometry and the spatial discretisation parameters must be provided. The MeshMaker module will then process the input and generate a mesh file that can be directly loaded by TOUGHREACT. When other mesh generators are used, the output data need to be rearranged in order to comply with mesh file format required by TOUGHREACT.

Standard output at user-specified simulation times or time steps is generated by TOUGHREACT. This output provides some time-stepping information, and a complete element-by-element report of thermodynamic state variables and other important parameters. Additional optional output is available on mass and heat flow rates, velocity fields, and on the diffusive fluxes of various other components. The software can print a file a format suitable for post-processing in Tecplot.

5.3   PFLOTRAN

PFLOTRAN solves a system of generally nonlinear partial differential equations describing multiphase, multicomponent and multi-scale reactive flow and transport in porous materials. The code is designed to run on massively parallel computing architectures as well as workstations (see PFLOTRAN project page, url provided in the references section).

The package contains several modules, briefly described in the following.

- RICHARDS: it solves the Richard's equation for isothermal problems solving equation (1). All the standard saturation and permeability function are implemented and can be selected from the input file. The RICHARDS module can be coupled to the Reactive Transport module.

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- MPHASES: it solves the mass and energy conservation equations for a multiphase system of n-phases. It can be coupled to the Reactive Transport module.

- 2PH: it solves for two phase liquid water-gas flow (mass and energy conservation) coupled to the Reactive Transport module.

- THC (thermal-hydrologic-chemical): it applies to single phase, variably saturated, non-isothermal systems with incorporation of density variations coupled to fluid flow. It can be coupled to the Reactive Transport module.

- CHEMISTRY (Reactive Transport): it solves mass conservation equations for the geochemical transport of a multiphase system. This is written in terms of a set of independent aqueous primary species (or components) (See section 3). The variables being transported are the total concentration of the primary species as for most standard geochemical reactive transport packages. Diffusion is assumed to be species independent, and the dispersivity currently must be described by a diagonal dispersion tensor. PFLOTRAN has an internal chemical database that can be edited to define customised chemical systems. Currently only the SNIA approach is available to couple the reactive and the transport term in Equation (6).

It must be said that PFLOTRAN is open source software under continuous development, and many of the features listed as not available are being implemented.

The control volume method is used to discretise the partial differential equations being solved and an UPWIND scheme is used to dump the instabilities rising from advection terms.

The problem definition parameters (such as hydrogeologic parameters, material constitutive relations, fluid properties), and numerical simulation parameters are passed to PFLOTRAN via ASCII data files. These files are manually adjusted by the end user in order to define the problem, and to tune the numerical solution for optimal accuracy / efficiency.

The computational mesh can be generated using the internal mesh generator using the keyword GRID or can be created using an external mesh-generation program adapting the mesh file format. Currently only hexahedral cell can be used to discretise the computational domain, soon prisms should be available too.

Visualisation of PFLOTRAN output must be performed via an external post-processing package. Since the source code for PFLOTRAN is freely available, any number of 3D visualisation packages may be used with only minor alteration to the source code. However, the freely available VisIt visualisation package (url provided in the references section) supports the native output of PFLOTRAN. Tecplot format can also be output if required.

5.4   Software overview summary

Features	HYDRUS-HP1	TOUGHREACT	PFLOTRAN
Multiphase	No	Yes	Yes
Chemical speciation modelling	Only for 1D problems	Yes	Yes
Variable density	No	Yes	Yes
Dual porosity	Yes	Yes	Yes
Layered soil	Yes	Yes	Yes

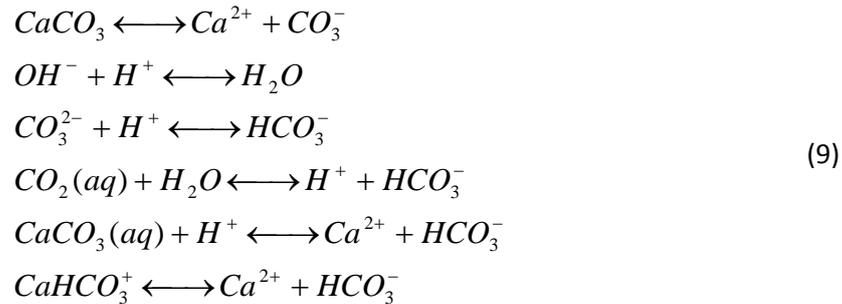|			
Heat transport	Yes	Yes	Yes
Parallel	No	No	Yes
Variable porosity	No	Yes	No
GUI	Yes	No	No
Pre-processor	Yes	Yes*	Yes*
Post-processor	yes	No	No

***Very simple mesh generator**

6   Software validation

The software validation is carried out increasing step by step the complexity of the problems solved:

  a)   saturated flow
      a.   Non-reactive transport
      b.   multi-species reactive transport
  b)   variably saturated flow
      a.   non-reactive transport
      b.   multi-species reactive transport
      c.   pure advective non-reactive transport
      d.   pure advective multi-species reactive transport

The chemical system chosen in this assessment is the dissolution of calcite, which is simulated in all the validation cases. Different cases correspond to different condition under which the dissolution take places (saturated/partially saturated flow, different pH values, etc). All the reactions are assumed to be at equilibrium and the porous matrix changes are neglected (this is a reasonable simplification due to the small amount of calcite that is expected to dissolve in the problems simulated). The chemical system describing the calcite dissolution is reported below:

$$
\begin{aligned}
CaCO_3 &\longleftrightarrow Ca^{2+} + CO_3^{-} \\
OH^{-} + H^{+} &\longleftrightarrow H_2O \\
CO_3^{2-} + H^{+} &\longleftrightarrow HCO_3^{-} \\
CO_2(aq) + H_2O &\longleftrightarrow H^{+} + HCO_3^{-} \\
CaCO_3(aq) + H^{+} &\longleftrightarrow Ca^{2+} + HCO_3^{-} \\
CaHCO_3^{+} &\longleftrightarrow Ca^{2+} + HCO_3^{-}
\end{aligned}
\tag{9}
$$

The set of primary and secondary species that have been chosen are shown respectively in (10) and (11):

$$
H^{+}, Ca^{2+}, HCO_3^{-}
\tag{10}
$$

$$
OH^{-}, CO_3^{2-}, CO_2(aq), CaCO_3(aq), CaHCO_3^{+}
\tag{11}
$$
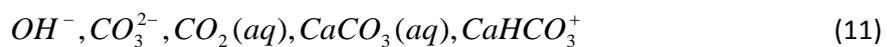
The calcite dissolution described by the first of the reactions (9) is driven by the following equilibrium constant (at 25° C):

$$\log(K_{CaCO3}) = -8.48 \qquad\qquad (12)$$

Local chemical equilibrium is assumed and the SNIA approach is used for the coupling of the reactive and the transport terms.

The time stepping is controlled by an algorithm that increases the time step size when convergence of the local chemical systems is achieved quickly (i.e. small number of non-linear iterations), and decreases the time step when the convergence requires a large number of iterations. Although this algorithm is implemented differently in the three software packages, it requires the same input parameters: initial, minimum and maximum time step; minimum and maximum number of local non-linear iterations; multiplier used to increase and decrease the time step. The initial, minimum and maximum time step passed to the software will be specified in the problem set up description, all other parameters are taken equal to the default values used by the software.

6.1   Calcite dissolution in a saturated flow

This case aims to replicate the first numerical experiments run with RETRASO in Saaltink at al. (2000). It considers the dissolution of calcite by sub-saturated infiltrating water in a one-dimensional domain. Initially the water is saturated with calcite.

Infiltrating a solution sub-saturated with respect to calcite (Fig. 1) additional calcite dissolution is observed due to the dilution of the initial solution. The dissolution can take place with a time scale that is much smaller than the one involved in the transport phenomena of the chemical species. In this case the dissolution reaction can be considered at equilibrium.

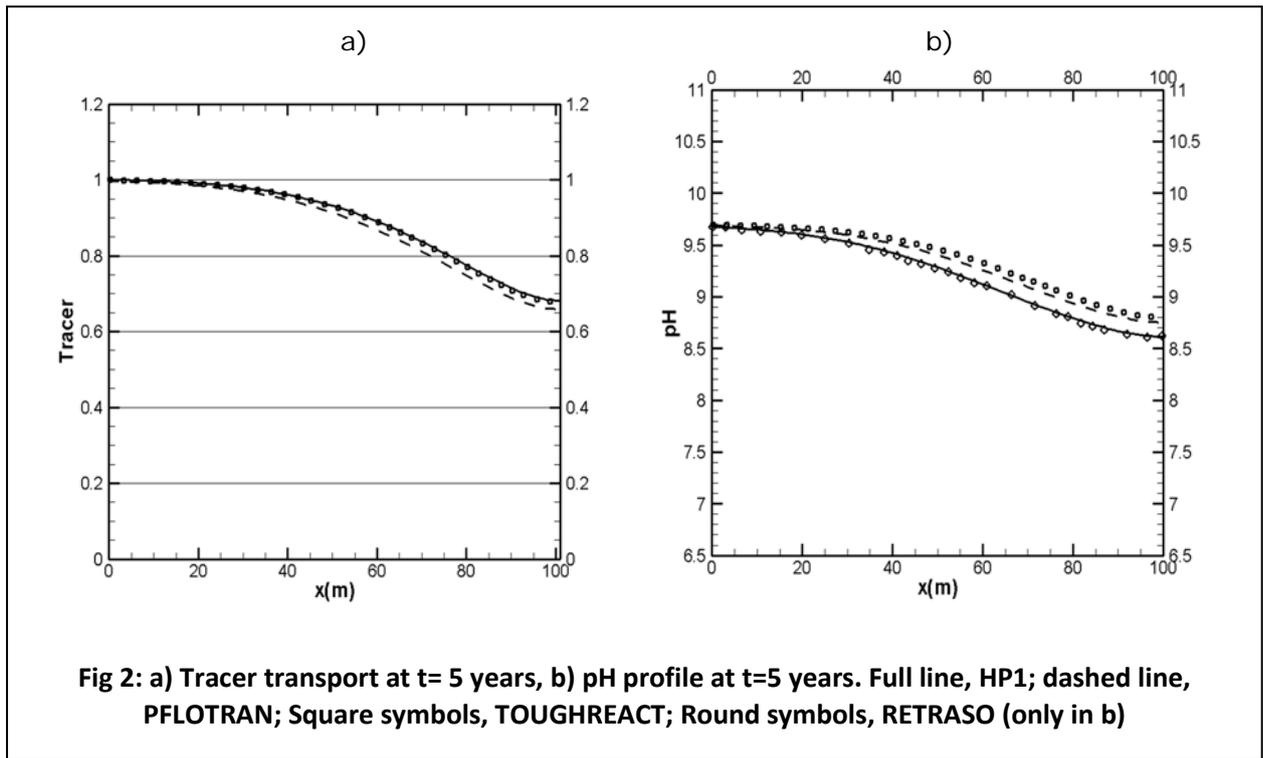**Fig 1: One dimensional domain: the infiltration point is on the left side**

The column is 100 m long, the soil porosity is equal to 0.1 and the longitudinal dispersivity coefficient is taken equal to 10 m. The sub-saturated solution is infiltrating with a rate of 2 m/year for 5 years.

The one dimensional domain is discretised using a uniform points distribution and a Δx=1 m. The time step input parameters are as follows: Δt_0= 0.0001 years, Δt_{min}= 0.0001 years, Δt_{MAX}=0.1 years
The boundary and initial conditions for the total concentrations are reported in the table below:

Total concentration	Initial Condition (*mol/ltr*)	Boundary Condition (*mol/ltr*)
H^+	pH=8.0	pH=5.5
Ca^{2+}	1×10^{-3}	$1 \times 10^{-4.398}$
HCO_3^-	1×10^{-3}	$1 \times 10^{-5.421}$

Table 1: BC and IC for the calcite dissolution in saturated flow

First the transport of a tracer is solved comparing the solutions obtained with the three software analysed for t= 5 years (tracer BC and IC are 1.0 and 0.0 respectively), see Fig 2-a). Then, the calcite dissolution problem described above is simulated, and the pH profile obtained at t =5 years are shown in Fig 2-b).

Fig 2: a) Tracer transport at t= 5 years, b) pH profile at t=5 years. Full line, HP1; dashed line, PFLOTRAN; Square symbols, TOUGHREACT; Round symbols, RETRASO (only in b)

The tracer solutions show very small differences. For the calcite dissolution case the pH profiles are also very similar. In addition the solutions computed are in good agreement with the results of Saaltink et al. (2000). The pH rises in response to the dissolution of calcite because CO_3^{2-} from dissolved calcite takes up H^+ while forming HCO_3^-. The small differences between the software can be reduced further increasing the mesh resolution, particularly in the inlet region where higher gradients are expected. For comparison purposes the grid used for this example is kept as coarse as the one used in Saaltink et al. (2000).

6.2   Calcite dissolution in a variably saturated flow

A 10m column of dry soil (loam) is infiltrated with a flow rate of 0.072 m/day (equivalent to 3mm/hour of water). The model is built with a vertical column where the aquifer water level is assumed to be at z=0, Fig. 3. The one dimensional domain is discretised using a $\Delta z=0.1$m and the experiment total time is 30 days. The time step input parameters used are: $\Delta t_0= 1 \times 10^{-5}$ days, $\Delta t_{min}=1 \times 10^{-5}$ days, $\Delta t_{MAX}=1 \times 10^{-2}$ days.
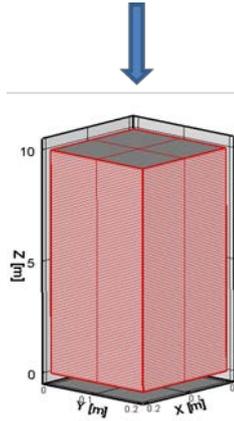
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Fig 3: vertical soil column with water infiltration at z=10m and aquifer water level at z=0 m. Δz=0.1m.

Van Genutchen permeability (13) and saturation (14) functions are used to represent the soil properties:

$$k_r = \sqrt{S_e}\left[1-\left(S_e^{1/\lambda}\right)^{\lambda}\right]^2 \tag{13}$$

$$S_e = \frac{S-S_r}{1-S_r} = \left[1+\left(\alpha P_C\right)^n\right]^{-\lambda} \tag{14}$$

Where k_r is the relative permeability, S is the water saturation, S_r is residual water, S_e the effective saturation. The following parameters are used in Eq. (13) and (14):

$$n = 1.26 \qquad \lambda = 0.359 \qquad S_r = 0.212$$

The porosity is taken equal to 0.43 and the permeability equal to 0.2496 m/day. Below the saturation evolution is shown comparing the solution obtained using the three software packages, see Fig. 4.
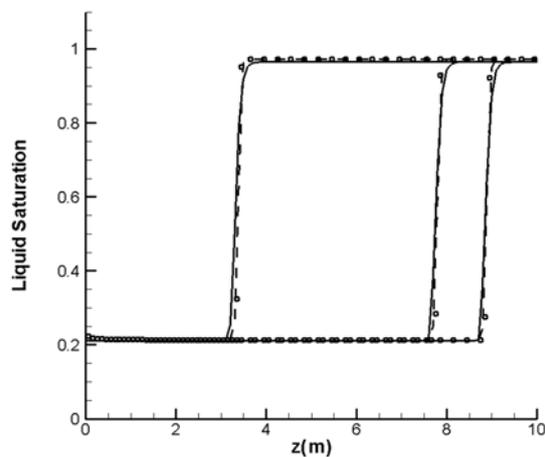

Fig 4: Saturation along the column at three instants: t=5 days, t=10 days, t=30 days.

HP1, PFLOTRAN and TOUGHREACT produce nearly identical solutions.

6.3 Calcite dissolution in a variably saturated flow with dispersivity

The water flux taken for this transport problem is the one generated from the previous flow simulation (section 5.2), and a longitudinal dispersivity coefficient equal to 1 m is adopted. The standard release of TOUGHREACT does not implement a dispersivity formulation (see section 4.2 for more details), and for this reason TOUGHREACT is not included in this comparison. As for the saturated flow test case, the non-reactive transport of a tracer is considered first to assess the software performance before introducing chemical speciations, Fig 5.
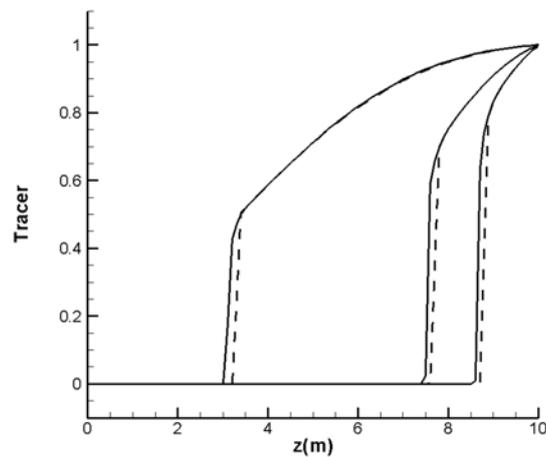

Fig 5: Transport of tracer in variably saturated water flow with longitudinal dispersivity coefficient equal to 1m. Profiles at three instants: t=5 days, t=10 days, t=30 days. Full line, HP1; dashed line, PFLOTRAN;

The HP1 and PFLOTRAN tracer solutions are nearly identical, with HP1 being slightly more diffusive. The chemical equilibrium speciations are then introduced for the reactive transport assessment. Two different set of boundary conditions are considered, while the same initial conditions are used in both cases, see table 2.

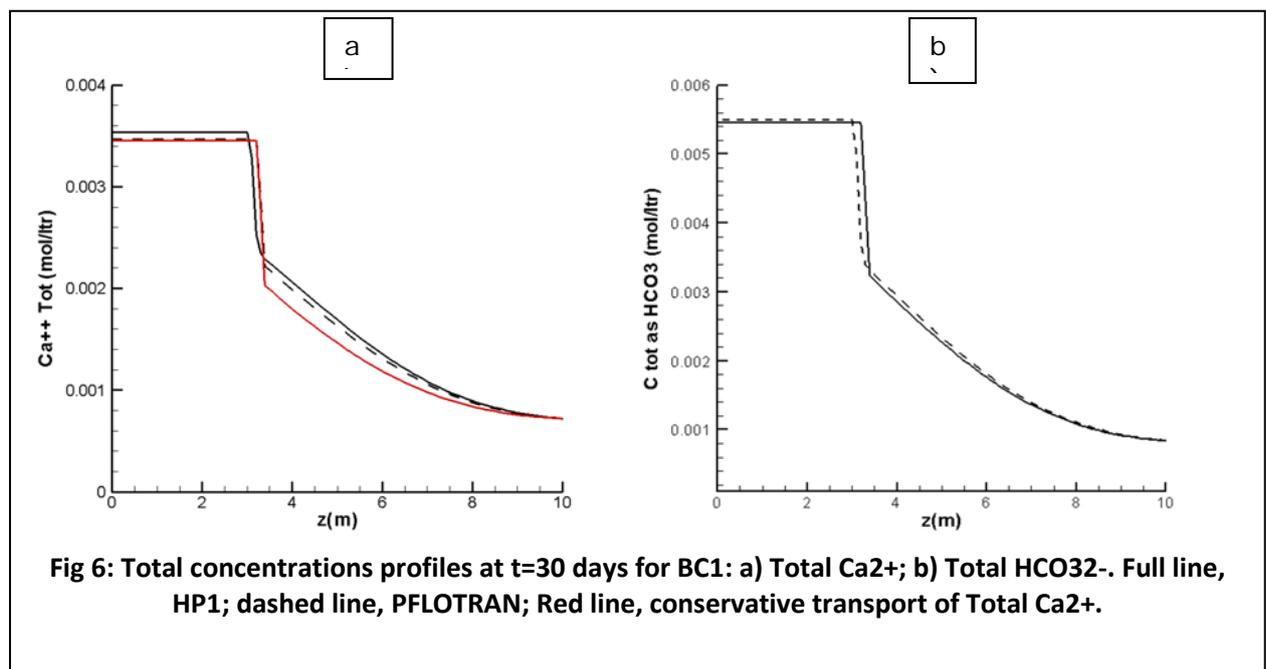| Total concentration	Initial Condition (mol/ltr)	Boundary Condition 1 (BC1) (mol/ltr)	Boundary Condition 2 (BC2) (mol/ltr)
H^+	pH=6.9	pH=8.2	pH=4.0
Ca^{2+}	2×10^{-3}	$7.195\times10^{-4.0}$	0
HCO_3^-	$P_{CO2}=10^{-1.5}$atm	$P_{CO2}=10^{-3.5}$atm	$P_{CO2}=10^{-3.5}$atm

Table 2: BCs and ICs for calcite dissolution in a partially saturated water flow

The carbonate total concentration is assigned imposing a pressure for the $CO_2(g)$, and the following reactions is adopted to translate the pressure in $CO_2(aq)$ molality (Appelo and Postama 2009):

$$CO_2(g) \longrightarrow CO_2(aq) \text{ with } \log(K_{CO_2}) = -1.468 \tag{15}$$

The $CO_2(g)$ pressures are chosen to reflect realistic values in the atmosphere ($P_{CO2}=10^{-3.5}$atm) and in the immediate subsurface ($P_{CO2}=10^{-1.5}$atm) where respiration and organic matter degradation causes higher level of $CO_2(g)$ pressure (Appelo and Postama 2009). A pH equal to 6.9 is taken for the soil of the respiration zone. Two types of infiltrating water are used in the numerical experiments: an infilling water with pH equal to 8.2 and a concentration of dissolved calcium obtained equilibrating the solution with a large amount of calcite (more than required to get a saturation index equal to 1), see Table 1 BC1; an infilling water representing an acid rain with pH=4.0 and no presence of calcium.

In Fig. 6 the distributions of the total concentrations of Ca^{2+} and HCO_3^{2-} are shown for t=30 days and BC1. In Fig 6-a) the non-reactive transport of the Ca^{2+} total concentration is also plotted. This is equivalent to the conservative transport of a tracer with the same initial and boundary condition of the Ca^{2+} total concentration.

Fig 6: Total concentrations profiles at t=30 days for BC1: a) Total Ca2+; b) Total HCO32-. Full line, HP1; dashed line, PFLOTRAN; Red line, conservative transport of Total Ca2+.

It can be observed the increase of Ca^{2+} dissolved in water due to the calcite dissolution; this is shown by the difference between the black lines and the red line in Fig. 6-a). Finally the pH profiles obtained with BC1 and BC2 are compared for t=30 days, Fig. 7. As expected the infiltrating water BC2 causes a larger dissolution of calcite, and consequently higher values of pH.
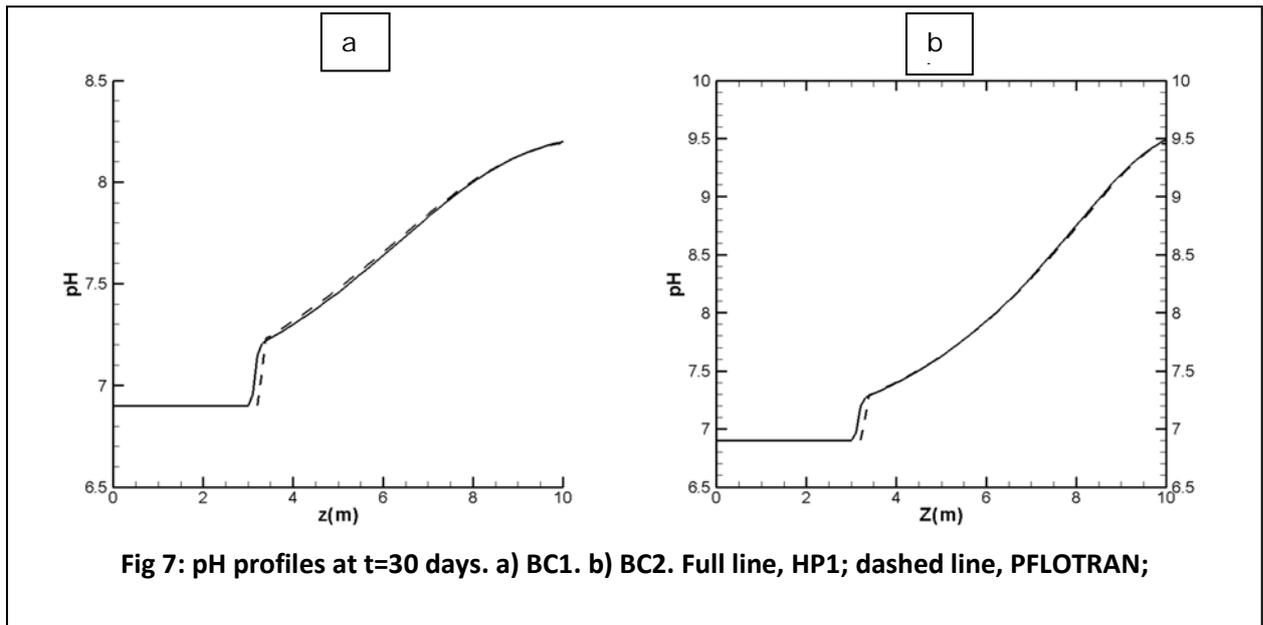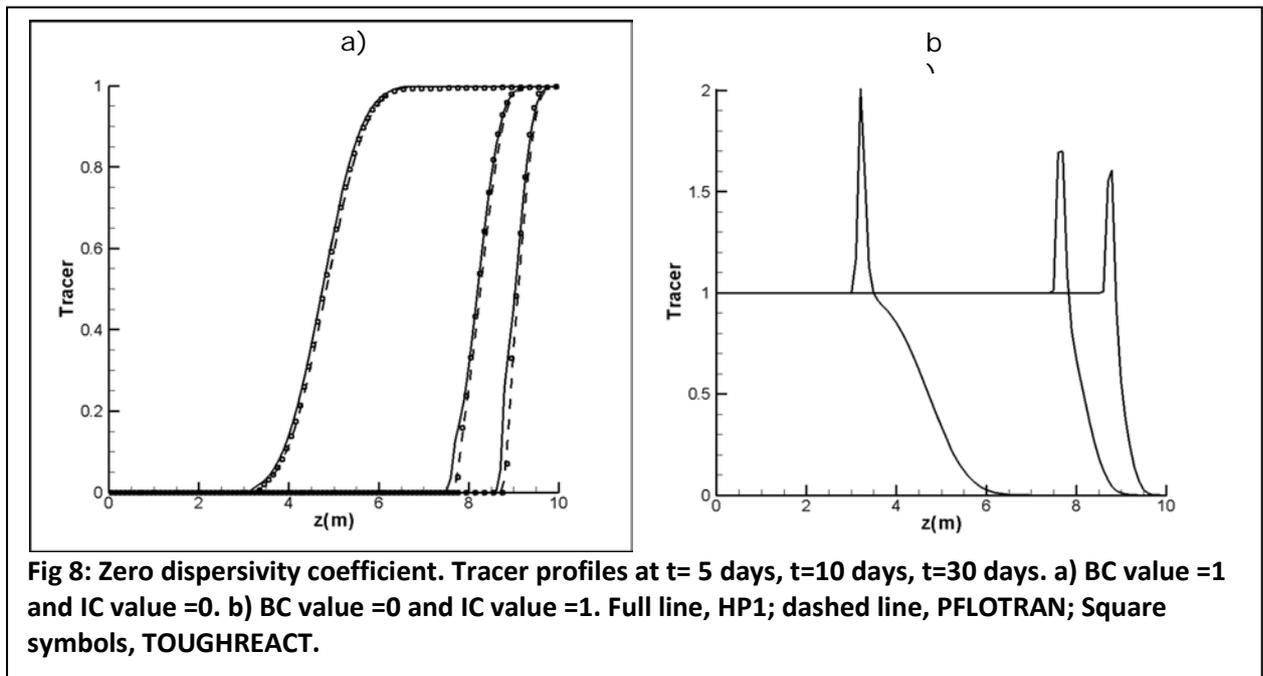
Fig 7: pH profiles at t=30 days. a) BC1. b) BC2. Full line, HP1; dashed line, PFLOTRAN;

Fig. 6 and 7 show very small differences between the HP1 and PFLOTRAN solutions.
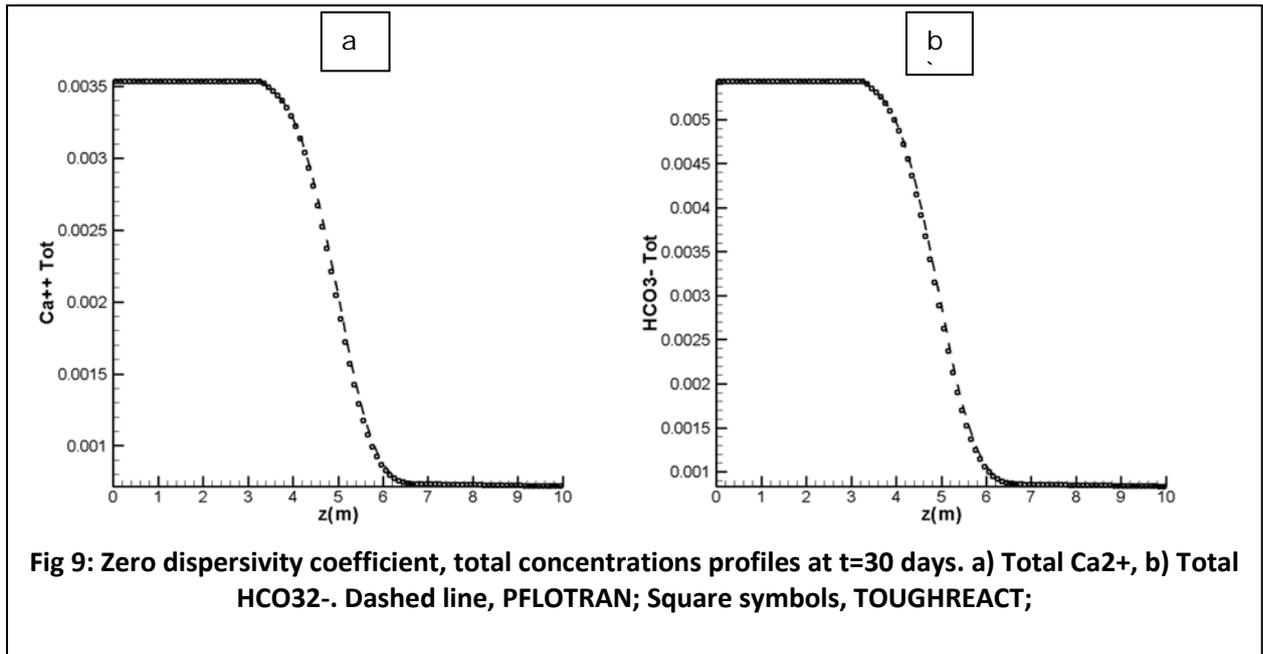
6.4   Calcite dissolution in a variably saturated flow with zero dispersivity

The same numerical experiment run in the previous section 5.3 is repeated imposing a zero dispersivity coefficient. This gives the opportunity to stress-test the software solving a pure advective transport problem. In addition TOUGHREACT, which does not implement the dispersivity in its reactive transport solution, can also be included in this comparison. The transport of a tracer is considered before including the chemical equilibrium reactions to investigate instabilities that might rise from the advective terms, see Fig. 8.

Fig 8: Zero dispersivity coefficient. Tracer profiles at t= 5 days, t=10 days, t=30 days. a) BC value =1 and IC value =0. b) BC value =0 and IC value =1. Full line, HP1; dashed line, PFLOTRAN; Square symbols, TOUGHREACT.

The UPWIND schemes available in the software tested are able to dump the instabilities in most of the circumstances, however HP1 shows a problem when the tracer is assigned a value equal to 0 as

BC and 1 as IC, Fig 8-b). In the same circumstance PFLOTRAN and TOUGHREACT still reproduce stable solution (not reported in this plot). The instabilities rising downstream the advective front in the HP1 solution, can be reduced increasing the mesh resolution, but they still exist when adopting a $\Delta z=0.01$. It seems not useful for the purpose of this comparison refining further the mesh, and HP1 is not considered in the next calcite dissolution example for which no dispersivity is included. Only the boundary conditions set BC1 of Table 2 are simulated and the total concentration distributions are shown in Fig. 9.

Fig 9: Zero dispersivity coefficient, total concentrations profiles at t=30 days. a) Total Ca2+, b) Total HCO32-. Dashed line, PFLOTRAN; Square symbols, TOUGHREACT;

The effect of the calcite dissolution on the Ca^{2+} dissolved in water is less visible compared to the case with dispersivity. For the sake of clarity, the comparison between non-reactive transport and the transport affected by the calcite dissolution of the total concentration of Ca^{2+} are show separately for each software package, see Fig 10.
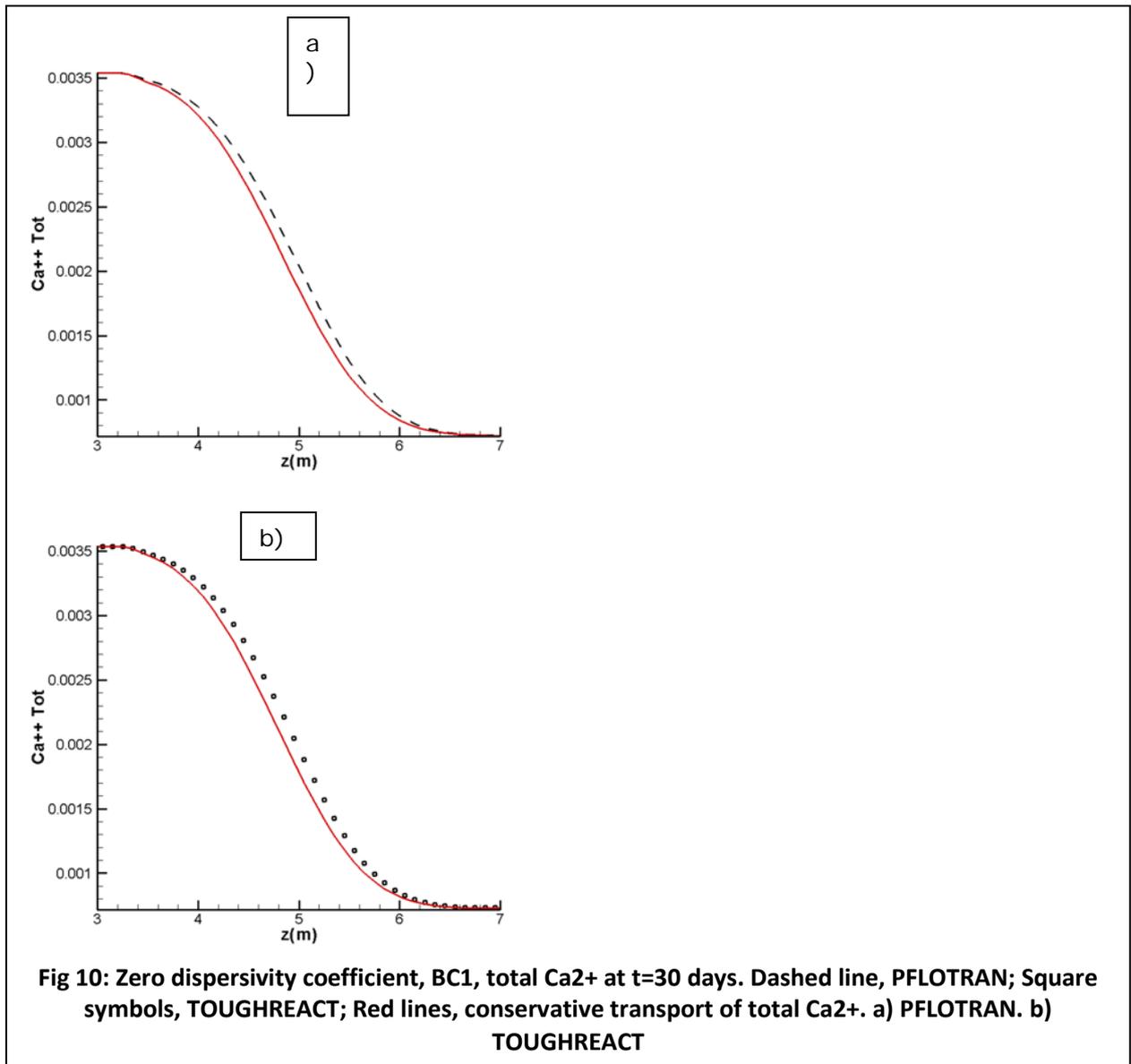
Fig 10: Zero dispersivity coefficient, BC1, total Ca2+ at t=30 days. Dashed line, PFLOTRAN; Square symbols, TOUGHREACT; Red lines, conservative transport of total Ca2+. a) PFLOTRAN. b) TOUGHREACT

Fig. 10 shows that both PLFOTRAN and TOUGHREACT indicate correctly an higher value of the total concentration of Ca^{2+} in the case of calcite dissolution.

Finally the pH at t= 30 days is compared in Fig 11 showing a very good agreement between the PFLOTRAN and TOUGHREACT solutions.
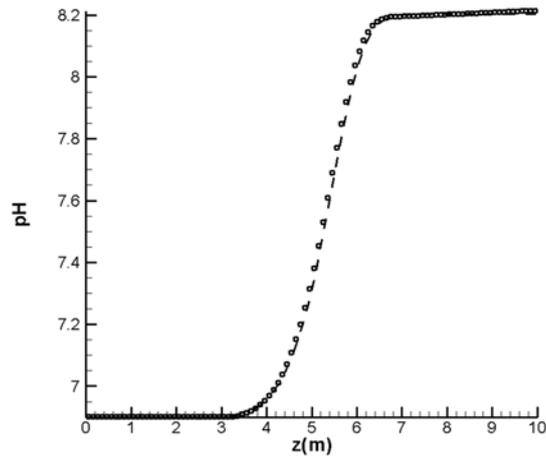
Fig 11: Zero dispersivity coefficient, BC1, pH profile at t= 30 days. Dashed line, PFLOTRAN; Square symbols, TOUGHREACT;

7   Conclusions

HYDRUS-HP1, PFLOTRAN and TOUGHREACT have been assessed for the solution of multi-species reactive transport problems in variably saturated water flow for applications in groundwater management and groundwater pollution control, and for the design and planning of artificial recharge with waters of different qualities. In this assessment, a calcite dissolution problem with all the reactions assumed to be at equilibrium has been considered. The solutions obtained have been compared showing a good agreement between the three software packages. HYDRUS-HP1 is the software with the best usability due to its intuitive GUI that guides the mesh generation, the problem set up and the post-processing. However, HP1 can model chemical speciation coupled to the solute transport only for one-dimensional problems. In addition the software has shown instabilities problems for pure advective transport problems. TOUGHREACT is with no doubt the software with the most complete modelling capabilities (if necessary special releases exist to include the dispersivity not considered in this report). The software is robust but its efficiency is limited by the lack of a parallel version for large scale problems. Between the software tested PFLOTRAN seems to be the most attractive software mainly for its parallel processing capability and robustness. In addition the software is open source and can account on a large number of people for future developments. On the other hand, PFLOTRAN still misses important modelling capabilities (e.g. unstructured meshes).

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