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3D stochastic modeling of flow and solute transport in karst vadose zone



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ABSTRACT

Predicting the outcome of a natural process is extremely difficult and challenging. Processes in the vadose zone are complex and transport of contaminants to the aquifers has been the subject of many previous research and models. It is possible to estimate water and pollutant transport in the unsaturated zone with many models, from simple to complex, developed over the previous few decades. More and more subsurface researchers and managers are using these models in their work. For more complex nonlinear systems, modelers can use numerical codes to account for many nonlinear processes simultaneously. Although simple problems can still be handled analytically or semi-analytically, numerical models have become significantly more common in recent decades as computing power has improved on both personal computers and supercomputers. These numerical models are accurate and stable, and they are frequently parallelized as a consequence. For the modeling of solute transport in the vadose zone, stochastic-convective (parallel soil column) and stochastic-continuum processes have been proposed. Neither of these models tackles 3D stochastic modeling of flow and solute transport in karst zones, as far as we know. In this work we will use the PhreeqcRM that is a reaction module for transport simulators based on the geochemical model PHREEQC. Then we develope a unique flowchart for the transport and flow of contaminants in karst vadose zone. A Matlab script finally implements the flowchart.

1. Introduction

Complex chemical reactions take place in the vadose zone when pesticides are present, [1,2]. Pesticide transport within soils and, in particular, how preferential flow through matrix and fractures, especially fracture vadose zone, affects the breakthrough of these compounds from vadose zone to groundwater are still not thoroughly understood, [3-6].

Advection diffusion equations, which are dominated by hyperbolic behavior, are commonly used to model the contaminant transport problem in variably saturated porous media. If we use first-order finite difference schemes to solve hyperbolic equations, we might see numerical diffusion near the fronts; if we use higher-order methods, we might see oscillations in the solutions. Time-dependent concentrations of contaminants can be predicted by using a linear advection diffusion equation. Because of these difficulties, this work uses a coupled Eulerian Lagrangian methods to solve the flow and contaminant transport problem in order to minimize numerical errors. Rather than solving the advection–dispersion equation directly, the approach of this work employs a Lagrangian perspective on the movement of solute particles within a flow field, while the fluid transporting solutes is integrated into system based on Eulerian control volumes. Reactive transport can be modelled using particle-based techniques. These methods have been particularly effective at assessing solute transport alone, [7–12]. Lagrangian fluid flow descriptions are already widely used and successful in fractured and heterogeneous aquifers. As an example, the continuous-time random walk (CTRW) technique takes into consideration the non-Fickian transport of tracer particles inside the water flow across heterogeneous, geological formations via multiple flow routes, each with an associated distribution of velocities and hence travel times, [13–15]. Despite this, Lagrangian modeling of fluid flow in the vadose zone is more difficult due to the temporally changing soil moisture levels and boundary conditions that influence the velocity field. Thus, only a few models use Lagrangian techniques to characterize the fluid phase itself for solute transport and water particles, [16–20].

In order to replicate non-reactive transport [21], postulated that these water particles might carry varying solute masses. Their Lagrangian Soil Water and Solute Transport Model (LAST) combines the advantages of the Lagrangian technique with a Euler grid to model fluid motion and conservative solute transport in 1-D soil domains that are heterogeneous and partially saturated. As a result, discrete water particles can move across the subsurface domain at various speeds and carry solute masses that are temporally variable. In Fig. 1 is given the principle of combining Eulerian and Lagrangian methods (see Fig. 2).

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Fig. 1. Principles of combining Eulerian and Lagrangian methods. **(A)** Eulerian current drives a random Lagrangian trajectory in a three-dimensional grid model (u, v, w). **(B)** A Lagrangian computation in the horizontal plane (w = 0) is depicted in the green box seen in (A) [22]). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

The vadose zone regarding the geochemistry is very complex. The vadose zone is known to play a critical role within the biosphere: (1) as a storage medium to supply water to the plants and atmosphere, and (2) as a controlling agent in the transmission of recharging water as well as contaminants from the land surface to groundwater, [23]. In Ref. [24] was reported that the average total dissolved solids values for rainwater changed dramatically from 30.2 mg/L at the land surface to 318 mg/L in groundwater. They also noted a corresponding change in the water type from a SO₄–Cl–Ca– NH₄ to a HCO₃–SO₄–Ca–Mg type due to vadose zone hydrogeochemical interactions. This and other studies document the significant role of vadose zone in contaminant distribution and migration, [25].

Advanced geochemical tools have been developed as a result of research into geochemistry generally like [26-29], among others. A wide number of environmentally important chemical processes can be simulated using these tools, but they are all Eulerian (grid-based) approaches. As a result, they all assume complete mixing at the cell size of the model, which is also the support scale for the mean velocity. The resolution of the model determines the amount of chemical variability that can be adequately simulated, although this does not rule out the use of Eulerian methods to analyze mixing limited reactive transport. Analyzing fine-scale heterogeneity in Eulerian models requires enormous processing times unless an upscaled model exists to bridge the scale differences between Eulerian and non-Eulerian simulations. Solute plumes and overall response rates can be incorrectly estimated using these methods due to numerical dispersion and false mixing during advective transport simulation, [30,31]. There has been a lot of attention recently on the significance of mixing on reaction rates, although these developments are mainly focused on elementary, bi-molecular reactions, [32,33]. Many of the assumptions required by the mathematical models can be limiting to the point that the approach or results of one study cannot easily be generalized to other reaction systems or initial conditions. These studies have led to great leaps in our understanding of mixing processes and their impact on reactions.

Much of the work on mixing has been done using Lagrangian methods, which have historically been employed for conservative transport or first-order decay, in contrast to geochemical research, [34]. Random walk particles' reactions can now be replicated in an increasing variety of ways, [35,36]. There have been a number of approaches to solving complex geochemical problems, such as multi-component transport, electrical or pH effects, speciation/complexation, and competitive reactions, but these have relied on simple reactions that are hard-wired into the solvers.

Due to the lack of robust particle-based alternatives, Eulerian-Lagrangian methods have a distinct advantage in simulating reactive transport to date. To the best of our knowledge, this is the first attempt to simulate stochastic flow and transport in karst vadose zone in 3D.

Our main goal of this work is to develope a unique Eularian Lagrangian flowchart to simulate flow and transport of contaminant in karst vadose zone, which passes through the following tasks.

- 1-) Setting up the initial and stochastic boundary conditions for the model (soil moisture and runoff).
- 2-) Formulation of the transient unsaturated flow model. Finite element formulations.
- Formulation of the stochastic Lagrangian transport in porous media.
- Matlab code was used to develop an upcaled technique for the 3D transmissibility field.
- 5-) Verification of our model against HYDROGEOCHEM 5.0 software

2. Methodology

1-) Setting up the initial and stochastic boundary conditions for the model (soil moisture and runoff).

Because stochastic soil moisture models are notoriously difficult to analyze, we devised three new approximations to this model that allowed us to generate ODEs that closely matched the seasonal trajectory of mean soil moisture and its associated pdf, that is soil moisture referred to as a water quantity indicator existing in soil and expressed as a percentage. On a daily level, there is a clear connection between soil moisture dynamics and seasonal trends. For starters, it saves time by not having to simulate rainfall input stochastically at each time step.



Fig. 2. Soil moisture patterns and pdfs have changed throughout the course of an entire year. Single realizations of stochastic soil moisture are represented in the equation by a single gray line. Their ensemble average is shown by the thick black line, while the dotted line indicates their time average over the course of a year. On the right side, a year-long pdf offers a snapshot, [37].



Fig. 3. In the left the concentration of particles at initial stage. Number of particles = 2700, in the right particle's concentration after t = 20-time unity towards positions, [42].

4-) Matlab code was used to develop an upcaled technique for the 3D transmissibility field of the Eulurian grid.

1-a Soil moisture dynamics

On a daily basis, rainfall pulses of varied depths replenish soil moisture, while evapotranspiration, leakage, and runoff drain the moisture from the soil, [37]. We overlook the importance of ground-water and focus solely on those systems that rely on surface water for their operation. We'll examine the 'effective' soil moisture, x, in the following section. There are two thresholds for plants: one is where x = 0 and the other is where all soil water is considered to have been lost through leakage and runoff, x = 1. These two extremes are within the range of x. The, s_1 threshold is typically found between field capacity and complete soil saturation. For x, we utilize the standard deviation of soil moisture s, which is equal to the sum of the standard deviation of $(s - s_w)/(s_1 - s_w)$. The rooting zone's effective soil moisture balance is as follows:

$$w_0 \frac{\mathrm{d}x(t)}{\mathrm{d}t} = \mathbf{R}(t) - \mathbf{ET}(x(t), t) - \mathbf{LQ}(x(t), t), \tag{1}$$

Soil porosity *n* and rooting depth Z_r are the variables in this equation that determine the maximal plant-available water storage capacity per unit ground surface, $w_o = nZ_r(s_1 - s_w)$. Evaporation, evapotranspiration and leakage/runoff, LQ(x(t), t) (cm per day) all contribute to the total

volume change of plant-available soil moisture, $(w_0(dx(t)/dt))$ (cm per day). A marked Poisson process, with a time-dependent rate parameter $\lambda(t)$ and an exponential distribution of mean (t) is used to model daily weather forecasts for rainfall, which is considered to be a time-dependent stochastic process. Rainfall patterns and other factors that affect evapotranspiration can contribute to seasonality. Some notation is required in the equation to distinguish between ensemble averages and temporal averages (1). This is due to the stochastic nature of all of the variables in equation (1).

A notation, $u(t) \in [u_{min}, u_{max}]$ is used to denote the average of the soil water partitioning variables in equation (1). All variables in equation (1) with a generic stochastic component can benefit from this. For any time-dependent pdf p(u, t), there is a $p_{ss}(u, t)$ associated with it that is generated by applying the instantaneous circumstances discovered at t over an extended period of time, until p(u, t), reaches steady state, generating $p_{ss}(u, t)$. On the other hand, we employ temporal averages, represented by overbars, which are calculated as follows: $\overline{u} = (1/T) \int_{t_0}^{t_0+T} where, t_0$ and t are the start and end times, respectively. Over a year ($T = T_{year}$), seasonal climate fluctuations occur, hence temporal averages of the ensemble average u(t) over this period are taken. The



Fig. 4. The Matlab code-generated Eluarian grid of upscaled transmissibility. Both colorbar graphs show that the upscaled values of transmissibilities before and after upscaling are of the same magnitude, hence the upscaling approach is the one we can utilize in simulations of the final results, [43]. Creating a unique flowchart for the transport and flow of contaminants in karst vadose zone.

temporal average over the course of a year will be identical to the longterm average if we neglect the early transients and solely evaluate the seasonally recurring stochastic process. Figure (3) schematically depicts the x(t), in gray, the pdf p(x, t) associated with them, and their ensemble average of x(t) in bold, as well as their long-term average in dashed (see Fig. 4).

The average soil moisture balance in Equation (1) can be normalized as follows:

$$\frac{dx(t)}{dt} = \frac{R(t)}{w_0} - \frac{ET(x(t))}{w_0} - \frac{LQ(x(t), t)}{w_0}$$
(2)

with the macroscopic equation taking into consideration the average rainfall effects as:

$$\frac{\mathrm{d}x(t)}{\mathrm{d}t} = \frac{\lambda(t)}{\gamma(t)} - \int_0^1 \frac{\mathrm{ET}(u)}{w_0} p(u,t) \mathrm{d}u - \frac{\lambda(t)}{\gamma(t)} \int_0^1 e^{-\gamma(t)(1-u)} p(u,t) \mathrm{d}u, \tag{3}$$

where $\gamma(t) = w_0 / \alpha(t)$.

It is possible to suppose that the average evapotranspiration across an area of heterogeneous soil and plants is linearly dependent on x, with a value of zero at the lower end of the scale and ET_{max} at x = 1 at the upper end. Evapotranspiration can now be simplified as follows:

$$\int_{0}^{1} \frac{\text{ET}(u)}{w_0} p(u,t) du = \frac{\text{ET}_{\max}(t)}{w_0} \int_{0}^{1} u p(u,t) du = k(t) x(t),$$
(4)

where $k(t) = \text{ET}_{max}(t)/w_0$ is the maximum value. A function's time dependency is indicated by a subscript *t*. Equation (3), which yield evapotranspiration, can be reduced to its simplest form.

$$\frac{\mathrm{d}x_t}{\mathrm{d}t} = \frac{\lambda_t}{\gamma t} - k_t x_t - \frac{\lambda_t}{\gamma t} \mathrm{e}^{-\gamma_t (1 - x_t)},\tag{5}$$

where

$$e^{-\gamma_t(1-x_t)} = \int_0^1 e^{-\gamma_t(1-u)} p_t(u) du.$$
 (6)

Because soil moisture, x(t) is unknown, the Soil Moisture Ensemble Averaging over Exponentiated Soil Moisture formula (5) is not closed. There exists a truncated Gamma distribution with parameters a and b under steady-state conditions for constant parameters, and the pdf of xas well as its ensemble mean are already known

$$p_{ss}(x) = \frac{b^a x^{a-1} e^{-bx}}{\Gamma(a) - \Gamma(a, b)}, \quad x_{ss} = \frac{a}{b} - \frac{b^{a-1}}{\Gamma(a) - \Gamma(a, b)} e^{-b},$$
(7)

where $a = \overline{\lambda}/\overline{k}$ and $b = \overline{\gamma}$ are constant values, and Γ (·, ·) indicates a truncated gamma function.

1-b Approximating the average leakage/runoff (LQ)

In order to calculate the leakage/runoff term, which in turn affects the evolution of mean soil moisture, it is necessary to have information on the whole pdf $p_t(x)$ at each time point. This information is missing from Equation (5), which makes it difficult to solve. The LQ term in this equation can be approached in four different ways, with the degree of difficulty increasing from one to four. These approximations can be used to estimate exact answers for x_t . As a starting point, let's look at scenarios where LQ_t can be ignored. Rainfall is supposed to be infrequent, with a low average depth of rainfall a_t and a large soil root depth, ω_0 to make this assumption. This is frequently the case in extremely dry regions or during the dry season. As a result of this, we have a more complicated formula for Equation (5).

4

 $\frac{dx_t}{dt} = \frac{\lambda_t}{\gamma_t} - k_t x_t, \tag{8}$

We can explicitly solve this simple ODE with an initial value of x_0 and an analytical solution of it if all parameters are considered to be constant.

$$x_t = \frac{\lambda}{\gamma k} + \left(x_0 - \frac{\lambda}{\gamma k}\right) e^{-kt},\tag{9}$$

When constant parameters are assumed, the stochastic differential equation (1), $p_t(x)$, can be solved. However, because there is no upper limit on the value of x_t these assumptions also lead to a large overestimation of x_t when leakage or runoff occurs. The following three examples are modern extensions of equation (5) that use various assumptions for $p_t(x)$ to approach. LQ_t.

So, for initial and stochastic boundary conditions, apart the traditional ones (Dirichlet, Neumann and Cauchy) we add a fourth boundary condition that is represented from the solution of the stochastic Equation (9) of the soil moisture (included in the flowchart below). For Dirichlet boundary conditions we have:

$$c(x, y, z, t) = c_0(x, y, z, t) \quad \text{for} \quad (x, y, z, t) \in \Gamma_d$$
(10)

At or near the Dirichlet border segments, c_0 is a predetermined concentration of [M L⁻³]. The term "concentration boundary condition" refers to the fact that this is a boundary condition that is commonly seen. The concentration flux at the boundary can be prescribed as follows using a Cauchy boundary condition of the third type:

$$-\theta D_i \frac{\partial c}{\partial x_j} n_i + q_i n_i c = q_i n_i c_0 \text{ for } (x, z) \in \Gamma_c$$
(11)

The entering fluid's concentration, c_0 , is represented by the outward unit normal vector, $q_i n_i$ [L T⁻¹]. A second-type (Neumann type) boundary condition, such as the following, can replace the Cauchy boundary condition when a border is impermeable ($q_0 = 0$) or water flow is directed away from the region.

$$-\theta D_{ij}\frac{\partial c}{\partial x_j}n_i = 0 \text{ for } (x,z) \in \Gamma_n$$
(12)

Cauchy boundary conditions are preferred over Dirichlet (or concentration) boundary conditions in the most majority of cases. This means that the solute flux into the transport domain will be known exactly (as specified) because Cauchy boundary conditions define the solute flux across the boundary. Advective and dispersive components of this specified solute flux are then separated in the transport domain. A Cauchy-boundary condition regulates simply the concentration on a boundary, but a Dirichlet boundary condition controls the solute flux, which is higher because of its advective and dispersive components. Particularly in the case of relatively short transport domains, the erroneous use of Dirichlet boundary conditions rather than Cauchy boundary conditions can lead to significant mass balance problems at an earlier period.

2-) The transient unsaturated flow model. Finite element formulations

The large-scale transient unsaturated flow model is given by:

$$C\frac{\partial H}{\partial t} = \frac{\partial}{\partial x_i} \left[K_{ij} \frac{\partial (H+z)}{\partial x_j} \right]$$
(13)

Mean pressure head (H), effective specific moisture capacity (C), and effective unsaturated hydraulic conductivity (K_{ij} .) are all defined in this manner: Soil property changes can be linked to changes in capillary tension head via a linear perturbation equation defined by Richard's effective parameter phase. Spectral analysis is used to determine the strength of correlations between changes in output and changes in soil property fluctuations in the effective parameters. Rewriting the wave fluctuation equation in the domain and using spectral representation qualities are applied.

The residual equation for each element is derived using the stochastic Galerkin method [38], applied to the large-scale transient unsaturated flow equation. The following findings are achieved by adding the element matrices using the direct stiffness approach:

$$[P]{H} + [S]{H} - {F} = 0$$
(14)

where [P] is the global capacitance matrix, [S] the global stiffness matrix, and $\{F\}$ is the global force vector.

Time-domain finite difference approximation is used to analyze the global system of equations, [37].

$$\begin{aligned} ([P] + \mathscr{B}(\Delta t)[S])\{H_{t+\Delta t}\} &= ([P] + (1 - \mathscr{B})(\Delta t)[S])\{H_t\} \\ + (\Delta t)((1 - \mathscr{B})\{F\}_t) + \mathscr{B}\{F\}_{t+\Delta t} \end{aligned}$$
(15)

For solving the above equation, (15) reader may refer to Refs. [39, 40].

3-) The stochastic Lagrangian transport in complicated porous media

Eulerian reactive transport techniques have long been the only option for simulating intricate geochemical systems. For modeling multicomponent reactions, here we employ the Lagrangian approach. Random walk-based methods for particle motion are used, but they allow the particles to interact by exchanging the mass of their chemical species with one other. A local disequilibrium is created, which is then relaxed into equilibrium using the reaction engine PhreeqcRM [41], by using the colocation density of each particle pair to determine the mass transfer rate. Particles only interact at the mass exchange stage; all other transport and response processes are performed independently of one another. Using an operator-splitting technique, PhreeqcRM is a geochemical reaction module designed to perform equilibrium and kinetic reaction computations. The reaction module's primary job is to use the transport simulator's model cells to obtain component concentrations, perform geochemical reactions, and then return the new component concentrations. An alternative to using component concentrations is to represent multicomponent diffusion (the Nernst Planck equation). PHREEQC's reaction capabilities are fully implemented in the reaction capabilities of the app. The reaction module ensures that the composition of all the reactants, including minerals, exchangers, surface complexers, gas phases, solid solutions, and user-defined kinetic reactants, is maintained in each of the cell's reaction chambers.

PhreeqcRM uses standard PHREEQC input definitions (files or strings) of chemical compositions of solutions and reactants to assign initial and boundary conditions to model cells. Reaction computations for inactive areas of a model domain can be eliminated using PhreeqcRM's additional features, including the ability to transfer concentrations and other model attributes.

Complex Reactions on Particles can be used to represent nonFickian transport in multiporous systems, [42]. Due to the discretization process, the total mass is divided into smaller pieces, with each piece representing a different proportion of the total mass. By avoiding numerical dispersion and oscillations, they avoid the typical Eulerian consequences. However, what happens if these particles interact chemically and kinetically? Transition probabilities can be used to address absorption reactions that are of a sluggish nature. These approaches can't be used to describe complex, nonlinear chemical reactions involving many different kinds of compounds. This is due to the fact that each time the concentrations are estimated. Many frequent geochemical processes are complicated, nonlinear, comprise multiple species and have extensive rock water interactions; this is a disadvantage. In this structure, each particle can be thought of as a unique water bin, with reactions occurring in the bins at different water concentration levels. Here's a quick rundown of the algorithm at work.

$$P(react) = P(react|colocation) \times P(colocation)$$
(16)

For more complex reactions, the following is the colocation probability:

$$P(s|\Delta t) = \int_{\Delta s} v(s|\Delta t) ds \approx v(s|\Delta t) \Delta s$$
(17)

There are two particles, separated by the distance s, the density function is given as v and t is the time. The density colocation function can be calculated using the formula below.

$$\mathbf{v}_{i,j}(\mathbf{s}|\Delta t) = \frac{\exp\left[-\frac{1}{4dt}\mathbf{s}^{\mathrm{T}}\left(\mathbf{D}_{i}+\mathbf{D}_{j}\right)^{-1}\mathbf{s}\right]}{\sqrt{\left(4\pi\Delta t\right)^{d}\det\left[\mathbf{D}_{i}+\mathbf{D}_{j}\right]}}$$
(18)

It is possible to express this relationship between velocity and mass in terms of an equation. This occurs when two or more particles are in close contact to one another.

$$m_{j}(t+\Delta t) - m_{j}(t) = \frac{1}{2} \sum_{i \neq j} (m_{i} - m_{j})^{*} v_{i,j}(s|\Delta t) \Delta s$$
(19)

Masses can be updated using the following equation:

$$\left(1 + \frac{1}{2}\sum_{i \neq j} \left(v_{i,j}(s|\Delta t)\Delta sm_j\right)\right) - \left(\frac{1}{2}\sum_{i \neq j} \left(v_{i,j}(s|\Delta t)\Delta sm_j\right)\right) = m_j(t)$$
(20)

Implementation of CPR MATLAB code. Reaction here for a simple case can be defined as:

$$\label{eq:cacoustic} \begin{array}{c} \mbox{Reaction: } CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} & & \\ \hline \\ \hline \\ \mbox{Equilibrium} \\ \mbox{Reaction: } CaCO_3(s) + & 2H^+(aq) \rightarrow Ca^{2+}(aq) + & CO_2(g) + \\ \hline \\ \mbox{H}_2O; & & \\ \hline \\ \mbox{Kinetic} \\ \hline \\ \mbox{kf} = 1.0; & & \\ \hline \\ \hline \\ \mbox{ki-} \end{array}$$

netic rate constant_____lam = 1e-3____Decay rate. A0 = 1.0; _____B0 = 1.15; _____B0 = 1.25; Initial concentration.

The water that drains from your home ends up in a septic tank, which is made up of a variety of different elements, including nitrate. This element is transported through buried pipelines under moderate pressure just enough to serve in our case, as a source of contamination. In some cases, these pipelines are damaged by corrosion or broken and so long part of them serve as contamination pipeline-segment, (in our case the length is 80 m).

3. Results (generating the MATLAB code with the graphical presentation)

There are three different fracture plane orientations that we have simulated in 3D using this methodology. The third fracture has a significantly larger aperture compared to the other two. This allows for greater practice. We first set up a cartesian matrix grid with dimensions $500 \times 200 \times 100$ m with grid blocks that are $10 \times 10 \times 10$ m. Matrix permeability is 150 mD and porosity is 35%.

HYDROGEOCHEM 5.0 [45], was used to test our Matlab code for the same issue as described above. It is possible to simulate fluid flow and biogeochemical kinetic/equilibrium reactions in saturated and unsaturated media using the computer program HYDROGEOCHEM 5.0. A three-dimensional version of the two-dimensional version of HYDRO-GEOCHEM 4.0 has been released. Fluid flow, heat transfer, and reactive biogeochemical transport equations are solved iteratively. An advection-dispersion-reactive-transport equation is solved for each mobile component equation and kinetic variable equation that has a kinetic coefficient greater than zero.

Our code and HYDROGEOCHEM 5.0 software yield similar results (the error ranges from 0.3 to 0.5 and from 0.9 to 1.1 1E-06 g/l) when compared to each other, for the duration of the simulation, 365 days. This could be explained in large part by the fact that our Matlab code uses the PhreeqcRM software, while the HYDROGEOCHEM 5.0 reaction engine includes heat transfer, a feature that our reaction engine does not.

5.b Transport model verification for simple numerical examples

HYDROGEOCHEM model can be used in simple cases like single horizontal plate or cross-shaped porous fracture to simulate fracture apertures and matrix system if small mesh sizes can be used to resolve them, [44]. In addition, the hydraulic conductivity differences between the fracture and matrix must be large enough to minimize the matrix's influence. According to the finite element method, the numerical dispersion of the HYDROGEOCHEM model developed in this study may be similar. A two-dimensional analytical solution developed by Ref. [46] is used in this study to verify the developed model's accuracy. Advection and dispersion in horizontal porous fracture plates are only compared.

A horizontal two-dimensional domain is the focus of the research. The simulation domain is similar to the first case we simulated. The author in Ref. [46] on the other hand, considers a uniform flow in the x-direction and constant values of longitudinal and transverse dispersion coefficients in the simulation domain. In Ref. [46] solution, the first-order decay is also a part of the transport process. There's a formula for the transport equation that follows:

$$\frac{\partial c(x,t)}{\partial t} = D_x \frac{\partial c(x,t)}{\partial x^2} + D_y \frac{\partial c(x,t)}{\partial y^2} - v_x \frac{\partial c(x,t)}{\partial x} - \lambda c(x,t),$$
(21)

with the initial and boundary conditions

$$c(x,0)|_{\Omega} = 0,$$
 (22)

 $c(x,t)|_{x=0,Y_1 \le y \le Y_2} = c_{\mathrm{D}},$ (23)

$$c(x,t)|_{x=0, y \le Y_1, Y_2 \le y} = 0,$$
(24)

$$\frac{\partial c(x,t)}{\partial x}\Big|_{x=\infty} = 0,$$
(25)

and

$$\frac{\partial c(x,t)}{\partial y}\Big|_{y=\pm\infty} = 0, \tag{26}$$

where v_x is the uniform seepage velocity in x direction, λ is the first-order decay coefficient for the model, c(x, t) is the concentration, and D_x , D_y are the longitudinal and transverse dispersion coefficients. As shown in the example, a concentration of c_D is applied between the Y_1 and Y_2 inlet boundaries (i.e., at x = 0). As a means of comparison, we have omitted considering the model's decay state. For example, the closed-form solution is obtained by using this approximation:

$$c(x,t) = \frac{c_{\mathrm{D}}x}{\sqrt{\pi D_x}} \exp\left(\frac{v_x x}{2 - D_x}\right) \$ \int_{\tau=0}^{\tau=t} \tau^{\frac{3}{2}} \exp\left[-\left(\frac{v_x^2}{4D_x}\right)\tau - \frac{x^2}{4D_x\tau}\right] \$ \left\{ \operatorname{erfc}\left[\frac{Y_1 - y}{2\sqrt{D_y\tau}}\right] - \operatorname{erfc}\left[\frac{Y_2 - y}{2\sqrt{D_y\tau}}\right] \right\} d\tau$$
(27)

Equation (27) necessitates numerical approximations in order to be calculated. The Gauss–Legendre iteration algorithm was proposed by Ref. [46] as a method for finding the solution. However, they found that iterations with a small x value were more prone to numerical errors.

A horizontal fracture plate and a cross-shaped fracture network (Fig. 10) are used in this example to test the developed transport model using the HYDROGEOCHEM model. Fracture sizes in the test cases are

Table 1	
Input parameters	[43],

Inlet pressure of injected nitrate	$P=1.03\times 10^6$
	$[kg \cdot m^{-1} \cdot s^{-2}]$
Fracture aperture (fracture 1 and 2)	$b = 0.0082 \ [m]$
Fracture aperture (fracture 3)	b = 0.66 [m]
Fracture spacing	$B = 0.085 \ [m]$
Fracture (sand) porosity	$\varphi_f = 0.38$
Matrix permeability	$k = 150 \times 10^{-12} [m^2]$
Hydraulic conductivity	K = 1 m/s
Matrix porosity	$\varphi_m = 0.35$
Fracture retardation coefficient	$R_{f} = 18$
Matrix retardation coefficient	$R_m = 24$
Effective diffusion coefficient of our contaminant arsenic	$D^* = 5.4 \times 10^{-9} m^2/s$
Overall release time of nitrate	$t = 5 \times 86400 \ [s]$
Contaminant boundary segment	$L = 80 \ [m]$
Volume of nitrate injected	1 [3]
Time of simulation	365 × 86400 [s]
Time step of simulation	$\Delta t = 3600 \ s$

Table 2

Flow and transport parameters used to verify the transport cases [43,44],

Fracture parameter	Case numerical	Case analytical
Western B.C	$\begin{array}{l}h=9.1 \text{ m}/\nabla c = \\0^{a}\end{array}$	$c_{\rm D} =$ 1.0 kg m ⁻³ (0.75 \le y \le 1.25) $c_{\rm D} = 0$ kg m ⁻³ (y $<$ Y ₁ , y $>$ Y ₂)
Eastern B.C	abla h = 9.0 m / abla c = 0	$\nabla c = 0$
Northern B.C.	$ abla h = 0 \ / abla c = 0$	abla c = 0
Southern B.C.	$ abla h = 0 \ / abla c = 0$	abla c = 0
Top B.C.	$ abla h = 0 \ / abla c = 0$	n/a
		$h = 9.01 \text{ m} (\text{ case } 2)^{\text{b}}$
Bottom B.C.	$ abla h = 0 \ / abla c = 0$	n/a
Fracture aperture (m)	0.001	n/a
K in fractures (md ⁻¹)	n/a	
K in matrix (md ⁻¹)	0.001	n/a
Effective porosity (-)	0.43	n/a
Seepage velocity (m day ⁻¹)	Variable ^c	$\nu_x = 0.1 \ m \ d^{-1} \ \nu_y \ = 0.1 \ m \ d^{-1}$
Isotropic dispersivity (m)	0.001	0.05
Time step (day)	0.1	0.1
Simulation time (day)	5.0	15.0

^a Fracture intersections with the western (or eastern) boundary of HYDRO-GEOCHEM and developed model are subjected to boundary conditions.

^b To the intersection of the vertical fracture and the simulation domain's top boundary, HYDROGEOCHEM and the developed model are subjected to the specified boundary conditions.

^c The Darcy flux at each node is used to determine the seepage velocity. Not applicable: n/a.

much larger than those in the controlled modeling domain. Fracture structures in HYDROGEOCHEM can only be generated with local mesh refinements in the HYDROGEOCHEM model (see Fig. 10a and c). Hydraulic conductivity values, on the other hand, are different for horizontal fracture plates (Fig. 3a) and cross-shaped fracture networks (Fig. 10a) (Fig. 10c). We assume a 0.001 m fracture aperture for the two test cases. The fracture plates in the developed model have a hydraulic conductivity of 1.0 md⁻¹. When using the HYDROGEOCHEM model, this value of fracture hydraulic conductivity is also applied to the elements that depict the fracture locations (Fig. 10a and c).

For fractures and the rock matrix, the hydraulic conductivity matrix in the HYDROGEOCHEM model has a wide range of values of 10^{-5} m d⁻¹. The effective porosity of the fractures in the test cases is a relatively large constant value of 0.43. The advection-dominated transport is evaluated using an isotropic dispersivity of 0.001 m. Except for the cross-shaped fracture network case, where a slightly upward flow along



Fig. 5. General flowchart, adopted from author of this work for general stochastic transport Lagrangian model + Eulerian flow model. In the left is represented the Lagrangian flowchart that mimics the stochastic complex reactions in fractured porous media, and in the right is represented the flowchart of the Eulerian flow model with stochastic inputs, that are; recharge, (that in previous section we have transformed in soil moisture), boundary conditions, hydraulic conductivity. Both the flowcharts are linked together in different steps for composing a unique model for stochastic flow and transport in fractured vadose porous media, [43].

the vertical fracture is introduced, the boundary conditions along boundaries parallel to the flow direction are specified as no-flow boundary conditions (Fig. 10c and d). As in the previous figures, the boundary conditions are exactly the same in Fig. 10c and d, but the top side of the vertical fracture (x = 1.0 and z = 1.0 m) is specified with a head of 9.01 m. A stress for upward flow in the vertical fracture can be



Fig. 6. A three-dimensional karst vadose zone with dimensions $500 \times 200 \times 100$ m and with their three principal fracture planes. In the right matrix-fracture planes discretization with tetrahedral elements where the rest of zone with the tetrahedral elements is not showed for not compromising the quality of figure, [43].



Fig. 7. The figure represents the result of the MATLAB code generation for the nitrates concetration, after t = 182.5 days. The lengths of three axes do not match the goal of observation, which is to better portray the figure. The nitrate contaminant source is represented with the red line-segment (the right-upper corner) of 105 m length. The nitrate volume under pressure in pipeline and the overall time of "injection" are $1m^3$ and 5 our respectively. After 5 hours the "injection" is interrupted (supposing that the pipeline that transport nitrate is repaired). From the figure it is notably clear the preferential flow through fractured planes, [43]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 8. The figure represents the result of the MATLAB code generation for the nitrates concertation, after t = 365 days. The simulation takes twice as long as the preceding figure. The lengths of three axes do not match the goal of observation, which is to better portray the figure. Nitrate concentration is certainly increasing, even though at first glance this increase appears to be smaller than expected, [43].

5 Model verification

5.a Model verification using HYDROGEOCHEM 5.0 software

produced by such a constant head of 9.01 on the top side of the vertical fracture. In these situations, the transport boundary condition is the Neumann boundary condition. A plume with a Gaussian distribution is released into the horizontal fracture plate in the test cases. Throughout the simulation period, a time step of 0.1 days is used for the transport simulation (5.0 days). The ADE solution method in the HYDRO-GEOCHEM model uses a Eulerian-based approach for comparison's sake, as does the transport solution in the developed model. Table 1 shows the test cases' flow and transport parameters (see Table 2).

The horizontal porous fracture plate in the following example measures 2×2 m in size. We proceed with the solution on the basis of the assumptions made in the Wexler study (1992). Concentration 1.0 is specified between $Y_1 = 0.75$ m and $Y_2 = 1.25$ m along the inlet boundary (i.e., x = 0) as the initial condition for this experiment. In the x-direction, the seepage rate is 0.1 m d⁻¹. The case has dispersivities of 0.1 m in both the longitudinal and transverse directions. For this dispersivity the scale-dependent dispersivity is used for the model to come up with this value. The study's scale of interest is about 1 m. Consequently, a dispersivity of 0.1 m was used for the transport simulation.

4. Discussion

A far higher concentration of nitrate may be expected from Figs. 7 and 8 than what is seen in the color bars of the two images, if simulation time was doubled from 182.5 to 365 days. In fact, the concentration slightly increased from 0.95 to 1 μ g/l. And this isn't just for no cause at all. Various physical, chemical, and biological factors govern the fate of dissolved nitrates as they pass through the vadose zone. This can be attributed to te very complex geochemical reactions in the vadose zone. Our code in Matlab uses the reaction engine PhreeqcRM module for complex reactions of Phreeqc software. In addition to diffusion and dispersion, chemical fate and transport in the subsurface can be affected



Fig. 9. The figure represents the result of the HYDROGEOCHEM 5.0 software simulation for the same problem described above, the nitrates concertation, after t = 365 days. The nitrate concentration simulated by HYDROGEOCHEM 5.0 software results in higher values, even than the differences with our Matlab code are small (respectively from 0.3 to 0.5 and from 0.9 to 1.1 E-6 g/l, see the colorbar scale). Due to the inability to change the color of the 3D figure in HYDROGEOCHEM 5.0, the colors of Figs. 8 and 9 are quite different. However, the values in the color bars for both figures are critical, [43]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 10. HYDROGEOCHEM model mesh for horizontal fracture plate, DFN model mesh for cross-shaped fracture network, and DFN model mesh for horizontal porous fracture are all used to verify the validity of a 2-D horizontal fracture plate and cross-shaped fracture network in this conceptual model. A single fracture plate (a) and cross-shaped fracture network (c) are both represented by relatively high hydraulic conductivity (1.0 m d^{-1}) in this model's HYDROGEOCHEM counterparts. However, in the HYDROGEOCHEM model, the hydraulic conductivity of the matrix was assumed to be 1 0^{-5} m d^{-1} , [43,44].

through solid-phase and biological sorption. Nitrates diffusion and dispersion are influenced by pore size distribution and concentration. As nitrate's dispersivity improves, so does its chemical dispersion, which results in a lower peak concentration. This could explain why the concentration of nitrates did not increase significantly despite the simulation time being doubled. Thus, the sorbed nitrates travels through the vadose zone more slowly than other noninteracting chemicals, with the degree of sorption heavily dependent on mineral type, specific surface area of the solid phase and organic matter content. In addition, cation exchange, mineral precipitation and dissolution complexes, oxidation reduction reactions, and transformations of contaminants are all examples of biogeochemical processes that alter contaminant concentrations (see Fig. 6) (see Fig. 5).

To make matters more complicated, each of these procedures is affected by variables such as ambient temperatures and pH levels as well as the degree to which water is saturated and the redox status of a system. The paradoxical' values (0.95–1 μ g/l) are maintained while water can take advantage of more accessible and less resistant channels, such as rock joints, fissures, and bedding planes. Even in materials that look to be homogeneous but aren't, preferential flow can occur, as seen in our case. Hydraulic conductivity is stronger in wetter soil, therefore even small changes in soil moisture might provide a favorable pathway for water flux. When it comes to plot-scale simulations, the last two figures reveal that vertical preferred flow is more relevant than lateral subsurface flow, which is well-known from prior studies. Nitrates concentrations drop as the distance from macropores in the matrix increases, according to the results of our Matlab code.

5. Conclusions

Using Lagrange's Complex Reactions and a stochastic FEM Galerkin for fluid flow, we were able to predict non-Fickian transport in multiporous systems, such as fracture rocks of the vadose zone. This is how we applied our Eulerian-Lagrange technique in 3D for the karst vadose zone. As a result of the high velocity and huge concentration gradients at and near fracture-matrix interfaces induced by rapid flow along fractures, matrix diffusion on matrix surfaces may be dominated by fractureflow enhanced diffusion according to the boundary-layer or film theory. Another finding was that in plot scale simulations, vertical preferential flow was more significant, whereas in catchment scale simulations, quick lateral subsurface flow is more significant, as is well-known. We demonstrated that Darcy's law equation can be used to directly apply hydraulic properties to numerical simulations. Also, we think that the preferred flow must be treated differently from nonpreferential flow (sometimes combined with a traditional Richard's equation for the matrix flow), which is a typical approach. Another important conclusion of the implementation of our algorithm in Matlab is that the results are in nearly in accordance with the HYDROGEOCHEM software.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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