New Fractional Hydro-Geochemical Model for Simulating Solutes Transport in the Soils at Unsteady State

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ABSTRACT

A new fractional hydro-geochemical model is proposed to simulate the transport and the speciation of solutes in the soil at steady state. Its purpose is to overcome several limitations of the classical advection dispersion model (ADE). A fractional ADE was used, coupled with a suitable geochemical model, and solved analytically. A MATLAB code was written for the new models and the well known transport models HYDRUS-1D and HP1 plus the experimental data were used for testing the applicability of the new model. The validation results showed that the new model well simulates the transfer of solutes and it is capable to provide more details about the species of solutes in the soil system.

RÉSUMÉ

Un modèle fractionnaire hydrogéochimique a été proposé pour simuler le transport et la spéciation des solutés dans les sols en régime permanent. L'objectif poursuivi est de remédier aux limitations du modèle classique d'advection dispersion (ADE). L'équation fractionnaire d'advection-dispersion (FADE) a été couplée sous MATLAB à un modèle de réactions géochimiques. Une solution analytique a été proposées et testée en la comparant à des simulations obtenues avec les codes HYDRUS-1D et HP1 et à certains résultats expérimentaux. La comparaison a montré que le nouveau modèle fractionnaire reproduit bien le transfert de solutés et qu'il est capable de donner plus de détails sur les espèces chimiques présentes dans le sol, sur leur migration et leur interaction.

1. INTRODUCTION

The advection – dispersion equation (ADE) is one of the most commonly used equations for describing the contaminant transport in the porous media. Many studies indicated that good results can be obtained with ADE to simulate the contaminant transport in homogeneous media. However, natural porous media and aquifers usually are heterogeneous. Accumulated researches showed that the traditional ADE associated with Fickian diffusion fail to describe the anomalous diffusion in heterogeneous media (Zhang et al. 2009, Huang et al. 2008, Roop 2008, Neuman and Tartakovsky 2008, Dawood I., 2007, and Zhang et al. 2007). The fractional advection-dispersion equation (FADE) is one of the promising way to simulate the non-Fickian transport process. The basic idea of the FADE is that the dispersion flux is proportional to the fractional derivative gradient of the contaminant concentration, and that the effect of the heterogeneity of the porous media on contaminant transport is reflected by the exponent of the fractional derivative.

To predict contaminant transport through the subsurface accurately, it is essential to develop a mathematical model taking into consideration the geochemical processes taking place in the soil, both between dissolved chemicals and solids, including soil particles. Most chemical reaction models are based on equilibrium conditions, and contain limited or no kinetic equations in any of their sub-models. Numerous reviews of chemical reaction codes have been published. Some of the most extensive reviews include those by Jenne 1981; Kincaid *et al.* 1984; Mercer *et al.* 1981; Nordstrom *et al.* 1979; Nordstrom and Ball 1984; Nordstrom and Munoz 1985; Potter 1979; and others. No single code can do all of the desired calculations in a perfectly general way. Jenne, 1981, divides chemical reaction codes into two general categories: aqueous speciation- solubility codes and reaction path codes. All of the aqueous speciation-solubility codes may be used to calculate aqueous speciation/complexation, and the degree of saturation of the speciated composition of the aqueous phase. Chemical reaction codes, such as WATEQ, REDEQL, GEOCHEM, MINEQL, MINTEQ, and their later versions, are examples of codes of this type. Reaction path codes include the capabilities to calculate aqueous speciation and the degree of saturation of aqueous solutions, but also permit the simulation of mass transfer due to mineral precipitation/dissolution or adsorption as a function of reaction progress. Examples of reaction path codes include PHREEQE, PATHCALC, and the EQ3/EQ6 series of codes. Some of the chemical reaction codes identified in the reviews by Goldberg, 1995, and Davis and Kent, 1990, as having adsorption models include HARPHRE (Brown *et al.*, 1991), HYDRAQL (Papelis *et al.*, 1988), SOILCHEM (Sposito and Coves, 1988), and the MINTEQ series of chemical reaction codes.

This study aims to developing a coupled fractional solute transport model and chemical equilibrium speciation model, which accounts for the hydro-geochemical interactions of contaminants with soils. The proposed models, suitably calibrated with experimental data, can help predict long term migration and retention of contaminants into the soils.

2. FRACTIONAL ADVECTION-DISPERSION EQUATION

The classical advection dispersion equation for a reactive solute transport can be expressed as (Bear, 1972):

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} \qquad [1]$$

where *C* is the solute concentration, D is the hydrodynamic dispersion coefficient, and v is the average pore velocity of solute transport. The fractional advection dispersion equation for a reactive solute transport can be expressed as (Benson, 1998):

$$R\frac{\partial C}{\partial t} = D\frac{\partial^\alpha C}{\partial z^\alpha} - v\frac{\partial C}{\partial z} \qquad [2]$$

where α is the fractional order which reflects the heterogeneity of soil ($1 < \alpha \le 2$). It is apparent that the classical ADE is a special case of the fractional ADE, where α = 2 (normal, or Fickian, diffusion).

Many authors (*e.g.* Benson 1998, Pachepsky *et al.* 2000, Huang *et al.* 2005, Meerschaert and Tadjeran 2004) have used FADE to successfully describe non-Fickian transport in soils at steady state (constant mean velocity), regardless of the effects of geochemical reactions on transport processes.

For steady state one dimensional transport with the initial and boundary conditions shown in Eq. 3, based on Benson (1998) and Benson et al. (2000), the analytical solution of Eq. 2 is given in Eq. 4:

$$\begin{aligned} &C(z,0) = 0 \qquad \text{for} \qquad 0 < z < \infty \\ &\left.\begin{aligned} &C(z,t) = C_o \qquad \text{for} \qquad z = 0 \\ &\frac{\partial C(z,t)}{\partial z} = 0 \qquad \text{for} \qquad z = \infty \end{aligned}\right\} \end{aligned} \qquad [3]$$

$$C = C_o\left[1 - \operatorname{erf}\left(\frac{z - vt/R}{\left(\left|\cos(\pi\alpha/2)\right| Dt/R\right)^{1/\alpha}}\right)\right] \qquad [4]$$

Where C is the concentration of the contaminant (ML^{-3}), C_o is the initial concentration of the contaminant (ML^{-3}), z is soil depth (L), v is the average pore velocity of contaminant transport ($L\,T^{-1}$), α is the fractional order, D is the dispersion coefficient ($L^{\alpha}T^{-1}$), t is time (T) and erf (x) is the error function:

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}\,dt \qquad [5]$$

3. THE GEOCHEMICAL REACTIONS MODEL

In order to describe the chemical reactions mathematically, a subset of the species must be chosen as components. All other ions, complexes, sorbed species and minerals can be formed from these components. It is assumed that all chemical interactions between soluble components in the aqueous phase and soil constituent in the solid phase are controlled by local equilibrium and that local equilibrium exists at every point of the system considered (MINTEQA2 1991). In the local equilibrium controlled transport system, the reaction rates are much faster than the rates of physical transport. This assumption may be the most restrictive relative to conditions that may pertain to the total system. The equilibrium chemistry must contain all of the phase-exchange and/or mass-equations necessary to describe the chemical processes affecting the transport, i.e. sorption, complexation, dissociation, and ion exchange. A system of n independent components that can be combining to form m species is represented by a set of mass action expressions of the form (MINTEQA2 1991):

$$K_i = \{S_i\}\prod_j X_j^{-a_{ij}} \qquad [6]$$

Where K_i is an equilibrium constant for the formation of species i, $\{S_i\}$ is the activity of species i, a_{ij} is the stoichiometric coefficient of component j in species i, Π indicates the product over all components in species i. The concentration of species i, $[S_i]$, is related to the activity $\{S_i\}$ by the activity coefficients γ_i

$$\{S_i\} = \gamma_i\,[S_i] \qquad [7]$$

Substituting this expression for $\{S_i\}$ in Eq. 6 and rearranging gives:

$$[S_i] = \frac{K_i}{\gamma_i}\prod_j X_j^{a_{ij}} \qquad [8]$$

Now if $K_i^{'}$ is defined as:

$$K_i^{'} = K_i / \gamma_i \qquad [9]$$

Then

$$C_i = [S_i] = K_i^{'}\prod_j X_j^{a_{ij}} \qquad [10]$$

In the logarithmic form, Eq. 10 becomes:

$$\log C_i = \log K_i^{'} + \sum_j a_{ij}\log X_j \qquad [11]$$

In addition to the mass action expressions, the set of n independent components is governed by n mass balance equation of the form:

$$Y_j = \sum_i a_{ij}C_i - T_j \qquad [12]$$

where T_j is total dissolved concentration of component j (known measured input parameter), Y_j is the differences between the calculated total dissolved concentration of component j and the known analytical total dissolved concentration of component j.

4. SOLUTION STRATEGY

For solving FADE at steady state, the master program first read the input parameters (such as pore water velocity and dispersion coefficient). This model furnishes the convected concentrations at each node which will be used for the next time step.

For the geochemical model, the solution (in the mathematical sense) is that set of component activities X (using matrix notation for brevity) which results in the set of concentrations C such that each individual of the set of mass balance differences Y is equal to zero (MINTEQ 1991).

In practice, it is only necessary to find X such that each individual of Y is made less than some tolerance value. The general procedure is to first guess X (makes this guess and puts it in the input file), then calculate C and Y. If any individual of Y exceeds (in absolute terms) its prescribed tolerance value, a new guess is made for X, C and Y are recalculated, and the test is repeated. This iterative procedure is continued until all the individuals of Y are less than the tolerance value. The Newton-Raphson approximation method is used to estimate the new X at each iteration. The tolerance value or convergence criterion is 10^{-4} times Tj for each component j. Solution processes for the geochemical model is shown in Figure 1. For the coupled model (geochemical-fractional model) ,The fractional advection-dispersion equation describing aqueous phase transport are spanning over spatial and temporal domains only, and the geochemical equations describing the transformation of contaminants into different species are spanning over the chemical domain only. In other words, the fractional ADE and geochemical equations are decoupled and solved separately. The advantage of this method of solution is that the highly non-linear behavior of geochemical equilibrium is confined to the model describing the geochemistry. Thus, the overall solution system consists of two steps: a physical step in which the fractional advection dispersion equation is solved, as transport term, and a chemical step in which the chemical equilibrium equations are solved for the aqueous and solid phase components for each nodal point in the spatial domain. A sequential coupling strategy of the physical and chemical steps has been adopted. The physical and chemical coupling is external. The disadvantage of this method is that chemical equilibrium is allowed to occur only at the end of each time step. This does not cause significant errors if small time steps are chosen.

Consequently, the master model first reads the physical and chemical input parameters. These parameters include: fractional order (α), pore water velocity (v), dispersion coefficient (D), time (t_o, Δt, t_{final}), depth (z, Δz), the considered aqueous species, the formation constants, pH, p_{CO2}, temperature, soil adsorption properties, and provisional total concentration of each component. At each time step, the master program calls the fractional transport model. This model furnishes the convected concentrations at each node for each component under consideration. The convected concentrations of the components are taken as inputs by the geochemical model. This model equilibrates the chemical system using the appropriate reactions and returns the modified component concentrations which are further convected by the fractional transport model at the next time step. The flowchart depicting this methodology is shown in Figure 2.

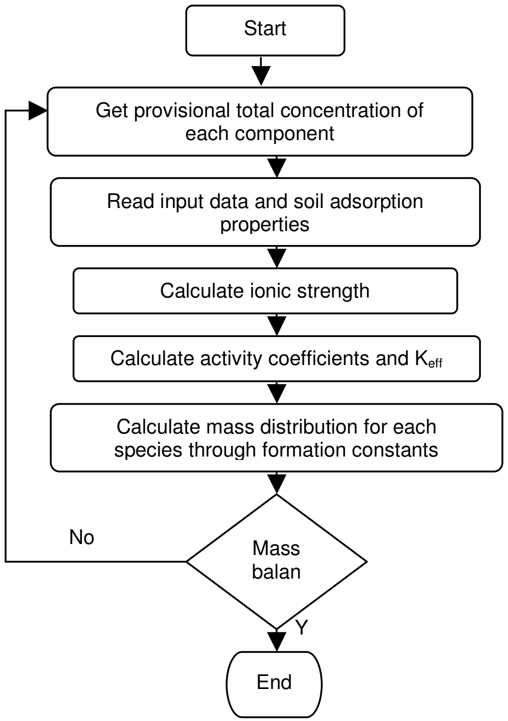

Figure 1. Flow diagram of the speciation sub-model

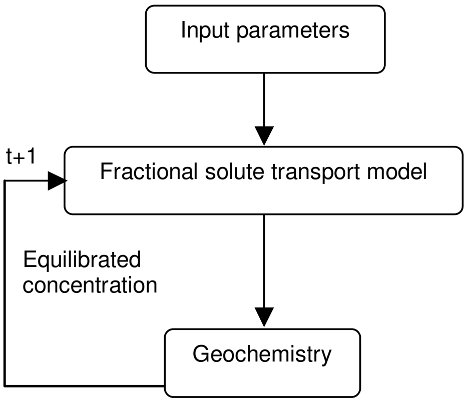

Figure 2. Flow diagram of GEO-STEFADE model solution

5. MODEL VALIDATION

Troide *et al.* (1995) measured chloride breakthrough curves with four electrical conductivity sensors at depths of 11, 17, 23 cm of a sand column. The experiments include leaching with solute free water during unsaturated conditions at $\theta=0.12$ and continuous application of 0.01M NaCl solution to an initially solute-free saturated sand at $\theta=0.3$. These data were used with the FADE parameters found in Pachepsky *et al.* (2000) (Table1), for the validation of our FADE code written in MATLAB.

Table1. Estimated parameters for FADE applied to data on Cl^- BTCs (Pachepesky et.al, 2000)

Data Source	Experiment	Column length (cm)	α	D_α (cm^α/hr)	v (cm/hr)
Troide et al., 1995	unsaturated	11	1.683	0.0305	0.258
	unsaturated	17	1.615	0.0291	0.255
	unsaturated	23	1.574	0.0282	0.25
	saturated	11	1.913	0.1518	2.452
	saturated	17	1.846	0.1224	2.514
	saturated	23	1.906	0.1073	2.506

Figures 3 and 4 show that the STEFADE model satisfactorily simulates the breakthrough curves in both saturated and unsaturated sand. The estimated parameters values (Table1) show that D, v, and α decrease when the length of column increases in the unsaturated sand. In the saturated sand, the values of v and α are approximately constant and D decreases when the length of column increases. Several values of α (1, 1.683, and 2) were used to simulate chloride transport in the sand column of 11 cm depth. From figure 5 one can notice that there is no significant difference between the simulation results with α = 1.683 and 2 in this case.

Experimental data of Cl^- transport in structured clay soil was published by Dyson and White (1987). The clay soil column (16.4 cm depth) was irrigated under flow rates of 0.28 and 2.75 cm/hr. A steady-state near saturated flow was created. Initial volumetric water content was 0.52 cm^3/cm^3, saturated water content was estimated as 0.67 cm^3/cm^3, and the steady state water content in soil column was 0.59 cm^3/cm^3. Soil was pre-irrigated with 10 mM $CaSO_4$ solution to reach the steady state water flow, and the step input of $CaCl_2$ was applied at the same intensity afterwards. Graphs were digitized to obtain data points. Pachepsky et al. (2000) calculated FADE parameters (D, v, and α) by the inverse method (Table 2). These data were used for the verification of our FADE model at steady state, STEFADE (Figures 6 and 7). These figures show that STEFADE with α = 1.642 well describes chloride transport in the clay soil. One can notice the significant influence of the numerical results. When α value decreases from 1.642 to 1, the normalized concentration (C/Co) decreases by approximately 50%. The estimated concentration increases by approximately 20% when α value increases from 1.642 to 2. The estimated values of α don't differ significantly for the two flow rates and are similar to those in the unsaturated sand. The dispersion coefficient (D) increases approximately 37 times as the flow rate increases 10 times.

Table2. Estimated parameters for the FADE applied to data on Cl^- BTCs from soil column (Pachepesky et.al. 2000)

Data Source	Experiment	Column length (cm)	α	D_α (cm^α/hr)	V (cm/hr)
Dyson and White, 1987	q= 0.28 cm/hr	16.4	1.642	1.209	0.756
	q= 2.75 cm/hr	16.4	1.695	44.69	12.89

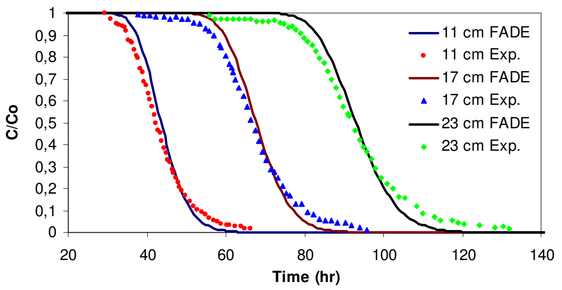

Figure 3. Comparison between measured and calculated chloride breakthrough curves in unsaturated sand.

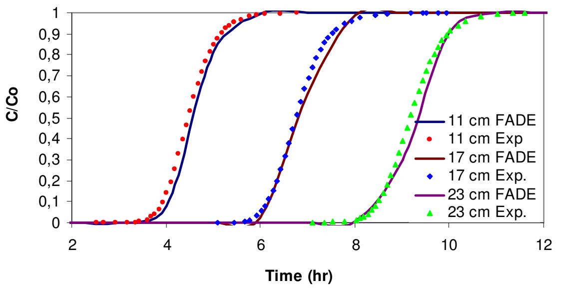

Figure 4. Comparison between measured and calculated chloride breakthrough curves in saturated sand.

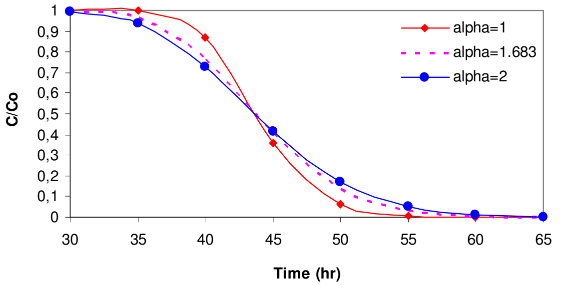

Figure 5. Chloride transport simulation in 11 cm soil column by FADE model with different values of α at the steady state.

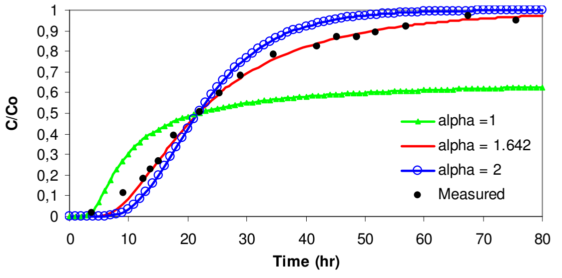

Figure 6. Comparison between measured and calculated chloride transport in the clayey soil with different α values and constant q = 0.28 cm/hr

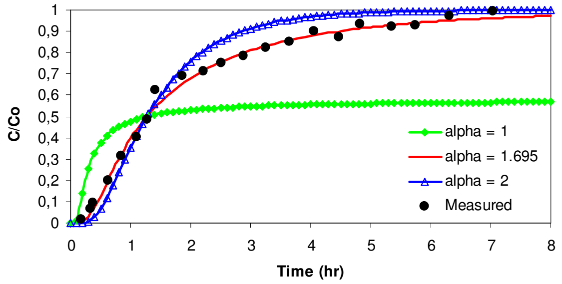

Figure 7. Comparison between measured and calculated chloride transport in the clayey soil with different α values and constant q = 2.75 cm/hr

5.3 VALIDATION OF GEO-STEFADE

For the validation of the coupled model at the steady state, results of cadmium transport on a sandy loam column of 15.04 cm diameter and 42.5 cm height made by Huang et al (2005) where used. The measured average pore velocity of steady state flow was 5.95 cm/hr and the cadmium concentration applied at the top of the soil column was 400 mg/l. The breakthrough curve of cadmium was used for determining FADE parameters at different soil depths (Table 3).

Table (3): Parameters for cadmium transport through a saturated sandy loam column (Huang et al 2005)

			(ADE)		
	depth (cm)		D (cm^2/hr)	v (cm/hr)	R
Saturated sandy loam	2		10.72	5.92	73.99
	7		9.25	5.97	48.53
	17		8.69	5.95	40.20
	27		6.10	5.93	57.55
	average		8.69	5.94	55.07
			(FADE)		
	depth (cm)	α	D (cm^{α}/hr)	v (cm/hr)	R
	2	1.54	7.22	5.95	37.06
	7	1.22	6.72	5.97	48.53
	17	1.94	7.75	5.96	41.12
	27	1.98	6.33	5.96	58.46
	average	1.67	7.29	5.96	46.29

Figure 8 shows a comparison of cadmium concentration calculated with STEFADE, the classical advection dispersion model and the measured data at 27 cm below the soil surface. This figure shows that STEFADE simulates cadmium transport in the soil better than ADE. From Figure 8, the amount of cadmium captured by the soil particles and the amount of cadmium passed with the liquid phase were known but without any details about the forms of the captured and passed cadmium species. Therefore, the use of FADE alone is insufficient for describing cadmium transport in the soil. The GEO-STEFADE model can be used for describing the transport of cadmium with respect to the geochemical aspects.

For the coupled model application, the system consists in: $[Cd^{2+}]_{total}$ = 0.712 mM, $[Cl^{-}]_{total}$ = 1.13 mM, $[SO_4^{2-}]$ = 0.781mM, $P(_{CO_3}{}^{2-})$ = 3mbar, pH = 5. The temperature was 25°C. Figure 9 shows the results of cadmium speciation. It can be observed that free cadmium ion $[Cd^{2+}]$ is the major aqueous species; it represents approximately 84% of the total cadmium concentration in the aqueous phase. While the concentration of cadmium carbonate $[CdCO_3]$ is approximately 10% of the total cadmium concentration in the aqueous phase. These results are related to solution pH (pH 5, *i.e.* acidic solution). To study the effect of pH on cadmium speciation, we changed the value of pH from 3 to 10 (acid to base). The simulation was done at 27 cm soil depth for 300 hours. The results are shown in Figure 10. They show that when pH value is less than 7, the major aqueous species of cadmium is free ion. When the pH value is between 7 and 10, the concentration of cadmium aqueous species decreases. When pH value is equal or greater than 10, the concentration of aqueous species is almost zero and most of the cadmium is converted to the solid phase. Similar results are obtained from HP1 with α = 2.

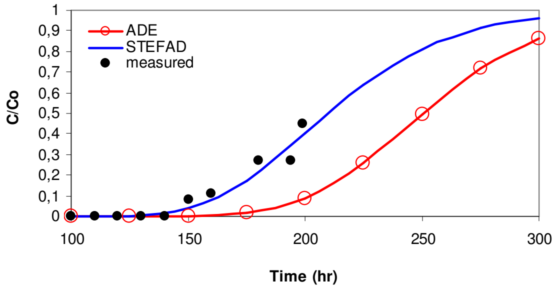

Figure 8. Comparison between FADE, ADE and data from Huang et. al (2005) at 27 cm soil depth

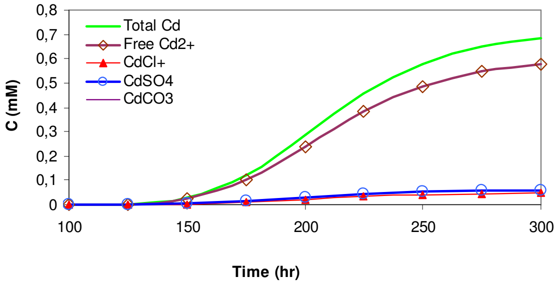

Figure 9. Cadmium aqueous species breakthrough at 27 cm soil depth and pH=5

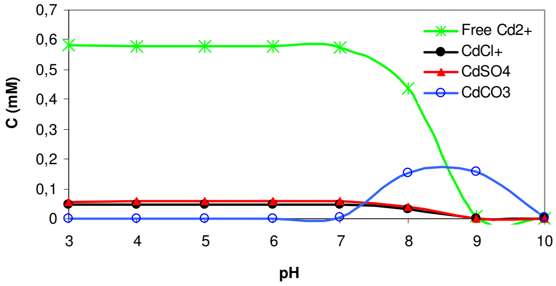

Figure 10. Cadmium aqueous species breakthrough at 27 cm soil depth after 300 hours for different pH values

6. CONCLUSIONS

Many published works show that the classical advection-dispersion equation (ADE) can not cover all solute transport problems. Therefore, the fractional advection-dispersion equation (FADE) was proposed to overcome the limitations of the classical ADE. In this study, the application of FADE at steady state was discussed and coupled with an equilibrium geochemical model. The coupled model was validated by comparison with the experimental data and the geo-transport code HP1. Comparison between experimental and simulated data of chloride transport in both sand and clay soil columns shows that FADE can simulate solute transport better than the classical advection dispersion model. Although no great difference between the classical ADE and FADE model simulation results were found for saturated sand, in a clay soil the value of the fractional order of derivation α was found to affect significantly the shape of breakthrough curves because of relatively high pore water velocity. The results obtained from the application of the GEO-STEFADE show its capability to give more details about the solute concentration and its species (forms) in the soil solution.

The coupling of an unsteady state FADE model (non uniform mean velocity) and the geochemical model will be published in a forthcoming paper.

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