PARADOXES AND DIFFICULTIES ASSOCIATED TO THE USE OF NON-LINEAR SORPTION ISOTHERMS ON THE NUMERICAL MODELING OF CONTAMINANT TRANSPORT IN GROUNDWATER

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Resumo - Isotermas de adsorção são extensivamente utilizadas na modelagem da interação de contaminantes de águas subterrâneas com a matriz porosa, bem como na predição do transporte destes contaminantes na sub-superfície. Isotermas não-lineares podem freqüentemente descrever melhor a adsorção em faixas de concentração mais amplas do que a isoterma linear. Apesar de a formulação matemática de modelos de transporte que empregam isotermas não-lineares ser razoavelmente simples, a solução por elementos finitos destes modelos pode sofrer de algumas dificuldades devido ao efeito não-linear da inclinação (derivada) da curva isoterma. A solução do problema de Freundich é particularmente difícil de lidar-se numericamente e apresenta alguns paradoxos conceituais. Este artigo discute os paradoxos físicos e as dificuldades numéricas encontradas na modelagem do transporte com adsorção não-linear. A literatura relevante no campo da matemática aplicada é aqui revisada e interpretada no âmbito da prática da engenharia ambiental, ajudando assim a identificar as causas das dificuldades na solução numérica destes modelos. Em seguida, são analisadas as dificuldades numéricas encontradas em abordagens alternativas de solução por elementos finitos (Galerkin) deste modelo de transporte na formulação baseada no campo concentração apenas. Demonstra-se aqui que a abordagem traditional demanda o uso de um limitante numérico para a máxima inclinação da isoterma. Contudo, esta abordagem resulta em predições errôneas e não conservadoras no caso de um cenário de contaminação de águas subterrâneas. Um esquema numérico iterativo baseado na secante da curva isoterma (esquema *fecs*), ao invés da derivada analítica, é essencial para o cálculo da inclinação da isoterma no temo de massa da equação de transporte. Um exemplo encontrado na literatura do transporte de um soluto orgânico utilizando diferentes isotermas que ajustam bem um conjunto de dados de adsorção foi avaliado com respeito às respectivas conclusões, utilizando o modelo de transporte que conserva massa desenvolvido neste trabalho. O presente estudo também ressalta a importância de utilizar-se

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uma expansão não-tradicional apropriada para o termo de massa, de forma a encontrar uma solução adequada na modelagem do transporte de um contaminante sujeito a isotermas de adsorção não-lineares. A abordagem tradicional resulta em resultados incorretos, que podem levar à super-estimativa to tempo de chegada de uma frente de contaminação e à perda significativa de massa de contaminante nas predições de modelos de transporte.

Abstract - Sorption equilibrium isotherms have been widely used to model the interaction of groundwater contaminants with the porous matrix and to predict their fate and transport. Non-linear isotherms can often provide a better description of sorption over larger solute concentration ranges than the linear isotherm. Despite the rather simple mathematical formulation of transport models that incorporate non-linear isotherms, the finite element solution of these models may lead to some difficulties due to the non-linear effect of the isotherm slope. The solution of the Freundlich problem is particularly difficult to handle numerically and poses some conceptual paradoxes. The present paper discusses the physical paradoxes and numerical difficulties found in modeling transport with non-linear sorption. The relevant applied mathematics literature is here reviewed and interpreted in the realm of the environmental engineering practice, helping to identify the causes of the difficulties in the numerical solution of these transport models. Then the numerical difficulties found in alternative approaches of the finite element (Galerkin) solution of the transport model in the concentration-based formulation are analyzed. The traditional approach is shown to require the use of a numerical limiter (‘cap’) for the isotherm slope. Yet, this approach leads to spurious, non-conservative predictions if a groundwater contamination scenario is modeled. A finite element chord slope (*fecs*) iterative scheme, rather than an analytical derivative, is required for the evaluation of the non-linear isotherm slope on the mass-term of the transport equation in order to obtain mass-conservative results. An example of the transport modeling of an organic solute using different isotherms that fit equally well a published set of sorption data was taken from the literature and the conclusions of that study are re-assessed using the mass-conservative transport model here developed. The present study highlights the importance of using an appropriate, non-traditional expansion of the mass-term for the accurate finite element modeling of the transport of a contaminant subject to non-linear equilibrium sorption. If the inappropriate traditional approach is used, spurious results can lead to the overestimation of the time of arrival of a contamination front and to the loss of a significant amount of contaminant mass in the transport model predictions.

INTRODUCTION

The fate of several classes of contaminants in groundwater is not only controlled by physical transport processes or by physico-chemical phenomena occurring within the aqueous phase, but also to a great extent by reactions occurring at interfaces between groundwater and other phases. These phases can be either minerals or organic matter that compose the solid matrix of the porous media, or interfaces between groundwater and other fluids, such as a NAPL or air in the unsaturated zone. The interactions that lead to interphase partitioning or the binding and release of solutes to these interfaces are termed sorption reactions. Over the years, several types of models have been used to describe sorption and its subsequent effects on groundwater transport. Traditionally, semi-empirical models, such as sorption isotherms, have been preferred in the groundwater literature to model and predict the interaction of groundwater contaminants with the porous matrix. Isotherms describe the equilibrium distribution of solute mass among the phases of an environmental system by relating the amount of solute sorbed (S) per unit mass of sorbing phase to the concentration of solute in solution (C) per unit volume of solution:

$$S = \psi(C) \tag{1}$$

Experiments to determine sorption isotherms for a given solute are typically conducted in batch systems at thermodynamic equilibrium. Data that relate S and C are then fit to a given isotherm model using either linear regression to log-transformed data, or nonlinear regression to the raw data. Kinniburgh (1986) reviews the most commonly used isotherm models and their proper fitting to experimental data.

The most common isotherms are the linear, Langmuir, and Freundlich isotherms, which have very often been used in environmental engineering practice. The linear equilibrium sorption has frequently been used, primarily because of its simplicity. A linear isotherm is easily incorporated into the groundwater transport equation, since it assumes a linear relationship between S and C, with a slope commonly known as the distribution coefficient (K_d):

$$S = K_\mathrm{d}\, C \tag{2}$$

Non-linear isotherms, such as the Langmuir and Freundlich isotherms, are often more appropriate to describe sorption of some groundwater solutes to solid surfaces of the porous matrix. In general, these isotherms can provide a better description of sorption over larger solute concentration ranges than the linear isotherm. The Langmuir isotherm can be mechanistically derived by assuming that: (i) all surface sites are identical and have equal adsorption energies and (ii) adsorption occurs until a monolayer of adsorbate forms at the solid surface (Weber et al., 1991). The resulting expression is:

$$S = S_{\max} \frac{K_{\mathrm{L}} C}{1 + K_{\mathrm{L}} C} \tag{3}$$

where $S_{\max}$ is the maximum sorption capacity of the porous medium and K_{L} is the reciprocal of the solution concentration at $S_{\max}/2$. At very low concentrations, the Langmuir isotherm tends to asymptotically approach a linear isotherm. The Freundlich isotherm is frequently used to model sorption of solutes onto surface sites with multiple energy levels, such as solids with several types of sites or heterogeneous solids, such as soils. The mathematical form of the Freundlich isotherm can be derived by taking the integral of a continuum of Langmuir isotherms with a normal distribution of adsorption constants (Sposito, 1984), and is given by:

$$S = K_{\mathrm{F}} C^{N} \tag{4}$$

where N is a constant, commonly between 0 and 1 for environmental contaminants, and K_{F} is the Freundlich adsorption constant. Although batch isotherms are strictly valid for systems in thermodynamic equilibrium, a state of local quasi-equilibrium can in some situations be assumed when modeling groundwater transport, thus considerably simplifying the model.

Despite the rather simple mathematical representation of transport models that incorporate non-linear isotherms, some difficulties may arise in the finite element solution of these models, since the calculation of the slope of the isotherm is needed. The occurrence of these difficulties depends on the degree of non-linearity, on the approach used to discretize the mass term of the transport equation, and on the numerical scheme for calculating the isotherm slope. Groundwater transport with Freundlich sorption is particularly difficult to handle numerically and poses some conceptual paradoxes. The present paper discusses the physical and numerical paradoxes found in modeling transport with Freundlich sorption. The numerical difficulties found in the finite element solution of the groundwater transport model subject to non-linear sorption in the concentration-based formulation are here analyzed, in analogy to the ideas introduced by Rathfelder and Abriola (1994) in the solution of the unsaturated flow equation.. The effect on the breakthrough curves and concentration profiles of two alternative approaches (traditional and non-traditional) for expanding the mass-term in the standard Galerkin method with linear basis functions are presented, and the environmental consequences of using the inadequate approach are examined.

Although a considerable amount of literature on the topic is found in the applied mathematics field, most of the results there presented were either asymptotic analytical solutions for large time, or finite difference solutions, or did not use a concentration-based formulation with finite element. By relating the most important features described in that literature to the difficulties found in the numerical solution, the present paper also interprets the results from the applied mathematics literature in the realm of the environmental engineering practice,.

The mass-conservative transport model here developed, which employs a Picard iterative scheme for evaluating the non-linear isotherm slope, is then employed in the prediction of transport of organic solutes in columns using sorption data published by Weber et al. (1996). The effect of the isotherm model selection on the behavior of the transport predictions is here analyzed, and their conclusions are re-assessed using the present results. The conclusions presented here highlight the importance of an appropriate expansion of the mass-term for the accurate solution of the transport equation with non-linear equilibrium sorption.

FORMULATION OF THE TRANSPORT MODEL

A finite element model that produces a mass-conservative numerical solution of the transport equation subject to linear or non-linear local equilibrium sorption is developed in this study. The one-dimensional form of the advective-dispersive-reactive (ADR) equation for the transport of a solute in groundwater systems is here analyzed in order to better isolate and identify the effects of the formulation and of the approach used for the mass term (or accumulation term) of the equation. The assumptions underlying the transport equation include constant porosity, velocity and dispersion coefficient, as well as no decay or other sources or sinks of the contaminant in a one-dimensional porous medium where the volume-averaging continuum assumptions can be applied. The resulting transport equation is then:

$$\frac{\partial}{\partial t}(nC)+v\frac{\partial}{\partial x}(nC)-D\frac{\partial^2}{\partial x^2}(nC)=-\frac{\partial}{\partial t}(\rho_b S) \qquad (5)$$

The local equilibrium assumption is generally valid when the interaction of the solute with the porous solid matrix occurs much faster than the rate that groundwater flows across the pore (Weber et al., 1991). In this case, sorption isotherms are often used to directly relate the concentration in the solid phase to the concentration in the aqueous phase at thermodynamic equilibrium. Thus, for constant and uniform porosity and constant bulk density, the transport equation (5) simplifies to:

$$R(C)\frac{\partial C}{\partial t}+v\frac{\partial C}{\partial x}-D\frac{\partial^2 C}{\partial x^2}=0 \qquad (6a)$$

where

$$R(C)=1+\frac{\rho_b}{n}\frac{\partial S}{\partial C} \qquad (6b)$$

$R(C)$ is here the retardation factor, and $\partial S/\partial C$ is the slope of the equilibrium isotherm, which can be linear or non-linear. For the nonlinear case, this slope can be the source of numerical difficulties.

Numerical methods such as the finite difference method or the finite element method are widely used in the solution of the partial differential equations (PDEs) that model the transport of contaminants in groundwater. Although it is in general expected that the numerical solution to the discrete version should converge to the solution of the original set of PDEs as the discretization grid is refined, this is not always true, especially in non-linear problems.

The amount of literature on finite element solutions of problem (6) is very limited. Yet, analytical solutions for simplifications of such a problem are found in the applied mathematics literature. These solutions provide an useful framework to study the difficulties found in the finite element solution, so they will be discussed in the below.

LITERATURE REVIEW

Nonlinear sorption can lead to the existence of moving concentration fronts of substances transported in porous media that do not change shape, depending on the value of the sorption parameters and on the time scale. The front spreading effects due to dispersion may be either enhanced or attenuated by the nonlinearity of sorption. In the case when sorption nonlinearity opposes the front spreading by dispersion, larger concentrations tend to move faster through the column than relatively smaller concentrations, resulting in a ‘self-sharpening’ or ‘compressive’ front. In the absence of dispersion, the self-sharpening nature of the resulting equation leads to a discontinuous ‘shock wave solution’. When dispersion is present, the self-sharpening effect of nonlinear sorption is counteracted by the dispersive effect and a continuous shock layer develops. As solute is transported and the opposing effects of nonlinearity and pore scale dispersion reach equal magnitude, the front ceases to flatten or steepen, eventually converging to a ‘shock layer’ or ‘traveling wave’ as $t\to\infty$. The asymptotic form of such a shock layer can be calculated by searching for traveling wave solutions that are steady state solutions in a moving coordinate system $\eta = x - \alpha t$. In this case, the resulting asymptotic traveling wave has a constant shape and moves with a velocity α with respect to the fix system. Mathematical analyses have frequently considered an infinite one-dimensional porous medium that is homogeneous with regards to the equation parameters (van Duijn and Knabner, 1991; van Duijn and Knabner, 1992b), since analytical solutions are available also the for nonlinear sorption cases. Although traveling waves describe in principle a limiting (asymptotic) behavior as $t\to\infty$, practical interest stems from the relatively fast convergence to traveling waves of the solutions of real problems.

Some authors have done a rigorous mathematical analysis, investigating the existence and uniqueness of traveling waves in the transport of solutes subject to nonlinear sorption. Rhee (1971) first studied traveling wave solutions for dispersive transport with Langmuir equilibrium sorption. van der Zee (1990), Boekhold (1990) and Bosma(1992) found the traveling wave analytical solutions for Freundlich sorption. van der Zee (1990) also developed expressions for the front shape, thickness, and position. They observed a non-Fickian type of behavior (as the front did not spread with the square root of time) and smaller front thickness on the nonlinear front when compared with the linear sorption case. They also noticed that when the initial concentration is greater than the injection concentration (such as when a contaminated aquifer is flushed with clean groundwater), a gradually spreading front is formed. van der Zee (1990) showed that the limiting traveling wave velocity (α) for a pulse injection depends only on the initial and injection concentrations and on the solute storage for this concentration increment in the sorbed and solution phases. Dispersion and nonequilibrium affect only the shape of the limiting traveling wave front, but not its velocity.

$$\alpha = \left\{ 1 + \frac{\rho_b}{n} \left[\frac{\psi(C_{lhs}) - \psi(C_{rhs})}{C_{lhs} - C_{rhs}} \right] \right\}^{-1} .v \qquad (7)$$

where C_{rhs} and C_{lhs} are concentrations of the downstream and upstream boundaries, respectively. van Duijn (1992a) and van Duijn (1992b) extended those results to the more general cases of nonlinear nonequilibrium sorption. Using a phase plane analysis, van Duijn (1991) developed a rigorous mathematical framework for the condition of existence of a traveling waves. They demonstrated that the existence of traveling waves for a contamination front is independent of prevalence or not of equilibrium conditions, but it is rather a global condition on the equilibrium isotherm, which can be interpreted geometrically as follows: a traveling wave exists if and only if, for all intermediate concentration values, the isotherm curve is above the chord of the isotherm between the concentrations of the downstream (C_{rhs}) and upstream (C_{lhs}) boundaries. This condition holds for strictly concave isotherms when $C_{\mathrm{lhs}} > C_{\mathrm{rhs}}$. van Duijn (1993) remarked that similar geometrical conditions also arise as entropy conditions in the theory for shock waves in first order hyperbolic equations. van Duijn (1991) also showed that desorption waves can be mathematically transformed onto adsorption waves by means of a simple substitution of variables. van Duijn (1993) investigated the Langmuir and the Freundlich problems and demonstrated that the latter always results in ‘traveling waves’ in a contamination pulse scenario if the Freundlich exponent $N \leq 1$. The solution of this case also features long tailings, due to the high sorption capacity at low concentrations.

The equation for transport with Freundlich isotherm has specific peculiarities that have deserved close attention from applied mathematicians due to the peculiar behavior of its solution. In their literature, transport (Eqn. 6) with Freundlich sorption is often classified as a 'degenerate parabolic problem' when the Freundlich exponent $N < 1$ (Grundy et al., 1994; van Duijn and Knabner, 1991). The degeneration of this problem is caused by the sorption isotherm not being Lispschitz continuous at $C = 0$, i.e., the Freundlich isotherm ($0 < N < 1$) is nondifferentiable for $C \to 0$, since $C^{N-1} \to \infty$. They also classified the transport equation (Eqns. 6) as 'uniformly parabolic' when $N \geq 1$ and 'degenerate parabolic' when $N < 1$. A consequence of the uniform parabolicity ($N \geq 1$) is that $C > 0$ everywhere in the domain for any $t > 0$, while the degenerate parabolic problem ($N < 1$) has a solution $C \equiv 0$ outside a disc of finite radius that expands in time ('bounded solution support') (Dawson et al., 1996). Thus, the singular infinite slope condition of the isotherm at $C = 0$ is sufficient to give rise to the 'finiteness' of the traveling wave (Gilding, 1989). van Duijn (1993) identified a more general sufficient condition for the finiteness of the traveling wave, which is that one of the contributions to the overall adsorption isotherm is non-differentiable for the value of the right-hand side boundary concentration. Gilding (1989) also identified that the solution support features 'instantaneous shrinking' in this case. This characteristic of the Freundlich solution contrasts with other parabolic diffusion and advection-dispersion problems (such as in the Langmuir isotherm, or Freundlich for $N \geq 1$) which feature an infinite wave exhibiting the paradoxical (physically inconsistent) property that mass is instantaneously distributed all the way downstream immediately after the injection of the solute at the upstream boundary, i.e., $C(x,t) > 0$ for any x, $t > 0$. The singularity in the slope and the subsequent finiteness in the Freundlich solution support leads to several interesting features that also impact the numerical solution.

Grundy (1994) developed large-time asymptotic analytical solutions for the Freundlich case and a finite solute pulse. In this case, there is a 'contamination front' (traveling wave) and a 'clean-up front' (rarefaction wave). Dawson (1996) extended that work to two spatial dimensions. Escobedo et al. (1993) obtained results for Freundlich with $N > 1$ for the three-dimensional problem, but not for $N < 1$.

Other asymptotic studies included Bosma and van der Zee (1993), who studied the first-order decay case with nonlinear Freundlich sorption in one dimension, deriving an asymptotic approximation based on a 'local traveling wave' type of solution. van Duijn (1997) incorporated the effect of decay in two-dimensional problems. Simon et al. (1997) analyzed a piecewise linear sorption isotherm. Vereecken et al. (2002) analyzed breakthrough curves and temporal moments for Freundlich, establishing a criterion to estimate the presence of the asymptotic regime in tails of experimental breakthrough curves (BTCs), and also to estimate the value of K_F for column data from the linear part (on a log-log plot) of the BTC tail.

Some numerical solutions have also been proposed, in general to compare with the asymptotic analytical solutions. van der Zee (1990) used a finite difference Crank-Nicholson iteration scheme and a very small ('negligibly small') initial 'background' concentration (C_{bkg} = 10^{-6}) for the numerical calculations. Jaekel et al. (1996), Jaekel and Vereecken (2002) and Vereecken et al. (2002) also used 'tiny background concentrations' to circumvent the singularity in the Freundlich slope, when using an explicit finite difference method. The small initial concentration that van der Zee (1990) used was required for their numerical solution of the Freundlich problem, but they also recognized that it was also the cause of discrepancy between their numerical and analytical solutions. In fact, as explained above, when small concentrations are initially present, the Freundlich problem becomes uniformly parabolic.

Bosma and van der Zee (1995) employed a mixed Eulerian-Lagrangian method that used particle tracking for advection and a finite-difference method for dispersion and also reported numerical difficulty originated on the nonlinearity of the Freundlich isotherm. Bosma et al. (1996) used a similar approach, but wrote the transport equation in terms of total solute concentration and defined a cell-averaged retardation coefficient, as opposed to the concentration-dependent retardation coefficient used by Bosma and van der Zee (1995). For that reason, they had to use a very fine spatial and temporal discretization. Abulaban et al. (1998) and Abulaban and Nieber (2000) also used a particle tracking technique in two-dimensions.

Dawson (1991) presented a general formulation of a time-splitting method for solving the transport equation in one dimension using a higher-order Godunov procedure approximation to advection and a mixed finite element procedure for dispersion. Dawson (1993) extended that analysis to multiple dimensions. Dawson et al. (1996) wrote the two-dimensional transport equation with nonlinear equilibrium sorption on the "conservative form", by first transforming it to a moving coordinate system ($\xi = t - x$) and making the change of variables to the total concentration ($c_{\mathrm{T}} = c + c^N$). Grundy (1994) also applied a finite difference scheme and a higher-order Godunov approach for the sorption term. van Duijn (1997) used the approach from Dawson (1991) and Dawson (1993) for the solution to the Freundlich transport problem with decay. However, the convergence of the numerical results to large time analytical solutions was extremely slow and impracticable for large t, so they introduced a change of variables that somewhat reduced this difficulty.

Dawson et al. (1994) developed a numerical procedure based on combining the method of characteristics with a Galerkin finite element method to model contaminant transport with nonlinear, nonequilibrium adsorption. Dawson et al. (1994) highlighted the nonstandard difficulty for this problem that arises when the isotherm is of Freundlich type and consequently the set $\{C > 0\}$ spreads at a finite speed through the flow domain. Knabner and Otto (2000) proved that the contraction principle of the support for the degenerate parabolic transport problem studied by

Gilding (1989) also happens for their weak form of those problems. They also demonstrated the uniqueness of these solutions for some problems, including the Freundlich case.

Barrett and Knabner (1997a; 1997b) described and analyzed a piecewise-linear Galerkin finite element approximation of a model for the transport equation with no advection, only diffusion. Dawson et al. (1998) analyzed the numerical approximation of the one-dimensional transport equation with Freundlich equilibrium sorption using a method similar to Barrett and Knabner (1997a; 1997b), but based on upwinding the advective term and solving diffusion using a mixed finite element method. Dawson et al. (1998) required a special treatment for the time-derivative of the transport equation. Aizinger et al. (2001) developed a Local Discontinuous Galerkin method, but only presented results for the Langmuir case. As they mentioned, their method requires that the element have a Lipschitz boundary, which is not the case for Freundlich.

As summarized above, the applied mathematics literature has analyzed extensively the transport problem with non-linear sorption. However, most of the work has been done on large-time, asymptotic solutions, since analytical solutions are available there. From those studies that also presented early-time numerical solutions, most were aimed at comparing with large-time analytical solutions for verification purpose, and did not report mass balance. Some numerical solutions used the finite difference method, where the non-linear coefficient is not distributed across nodes; others introduced ‘background concentrations’ to circumvent the dramatic effect of the non-linear coefficient.

In the groundwater literature, some studies have discussed the mass balance problems inherent to the numerical solution by finite elements or finite difference of the unsaturated flow equation (Abriola and Rathfelder, 1993; Celia et al., 1990; Pan et al., 1996; Rathfelder and Abriola, 1994; Woods et al., 2003), and non-linear transport equation (Huang et al., 1998). Due to the formal similarities between these two equations, particularly with respect to the nonlinearity in the mass term, the numerical solution of the unsaturated flow equation will be discussed first, as it provides the basis for solving the mass conservation problems in the transport formulation.

The traditional head-based form of the Richards equation for the unsaturated flow has been known to yield poor numerical solutions with large mass balance errors. Celia et al. (1990) showed that the solution of the mixed form of the equation can be mass conservative. Numerical procedures for efficient mass conservative solutions of the head-based form of the Richards equation were later presented by Rathfelder and Abriola (1994). They showed that the cause of the mass-balance errors in previous solutions was traditionally the inappropriate expansion of the capacity coefficient in the mass term of the equation. For the solutions to be mass conservative, the capacity coefficient had to be evaluated using the standard chord slope approximation for both finite element and finite difference methods. In addition to that, for the finite element method a nontraditional expansion of the mass term had to be employed, which preserved the equivalence of the elemental approximation of the moisture content time derivative only when the capacity coefficient was evaluated using the standard chord slope. Abriola and Rathfelder (1993) also discussed the effect on the mass balance accuracy and computational work of specifying a ‘cap’ on the capacity coefficient, in order to avoid a numerical singularity as the capillary pressure approached zero.

In order to obtain a mass-conservative solution for the nonlinear transport equation, Huang et al. (1998) extended the mixed formulation concepts from Celia et al.(1990). They employed a ‘mixed form’ of the transport equation, written in terms of total concentration, for the accumulation term, and aqueous concentration, for the other terms. Then, the total concentration from the accumulation term was expanded in Taylor series with respect to the solution concentration. The resulting ‘solute capacity coefficient’ (usually called elsewhere ‘retardation factor’) was calculated using a Picard iteration scheme. The other terms of the transport equation were expanded with a conventional finite element method. Huang et al.(1998) evaluated the performance of their mixed formulation against the traditional Picard (concentration-based) formulation, by simulating the Langmuir-Freundlich adsorption case. They reported a very good mass balance, in contrast with the standard concentration-based formulation with the traditional expansion of the mass term, which presented very poor mass balance for the nonlinear case. Huang et al.(1998) based their solutions on the ‘mixed form’ of the transport equation, but they did not seem to appreciate the possibility of also obtaining a mass-conservative solution for the concentration-based formulation of the transport equation. The present study introduces a mass-conservative solution for the concentration-based formulation of the transport equation by using the finite element chord slope scheme (*fecs*) for the calculation of the isotherm slope, in combination with a non-traditional approach for expansion of the mass term.

NUMERICAL DIFFICULTIES ASSOCIATED TO TRANSPORT

The numerical solution of the nonlinear problem given by equation (6) subject to appropriate initial and boundary conditions presents difficulties that are not found in the linear case. A cause for numerical difficulties in the solution of the transport equation with local equilibrium non-linear sorption stems from the behavior of the nonlinear retardation factor (Eqn. 6b), which is dominated at low aqueous concentrations by the slope of the non-linear isotherm ($\partial S/\partial C$). Although in the case of linear sorption this slope is simply given by K_d, in the Freundlich case it is given by:

$$\frac{\partial S}{\partial C} = NK_F C^{N-1} \qquad (8)$$

And in the Langmuir case:

$$\frac{\partial S}{\partial C} = S_{\max} \frac{K_{\mathrm{L}}}{(1 + K_{\mathrm{L}} C)^2} \tag{9}$$

Figure 1a presents an example of experimental fits of linear, Langmuir and Freundlich isotherms for the sorption of a non-ionic surfactant, polyoxyethylene (20) sorbitan monooleate (Tween 80) onto Ottawa 20-30 mesh sand in batch reactors (Weber et al., 1996). Weber et al.(1996) fit the Freundlich, and Langmuir models to this set of data using non-linear regression over the entire concentration range, from 5 to 500 mg/l, as well as a linear model in the range of 5 to 100 mg/l. Both non-linear isotherms fit well the data (Fig. 1a), and the linear isotherm provided a reasonable representation of the data up to about 70 mg/l. Figure 1b shows the computed retardation factors (Eqn. 6b) based on the reported parameters. The behavior of the slope of non-linear isotherms and its subsequent influence on the retardation factor of the transport equation warrant a special numerical treatment for the mass term in the finite element solution of equation (6a). Two major problems have been identified on the present study as sources of numerical difficulties of the concentration-based formulation of the transport equation: the magnitude of the slope itself and the numerical scheme for calculating the isotherm slope.

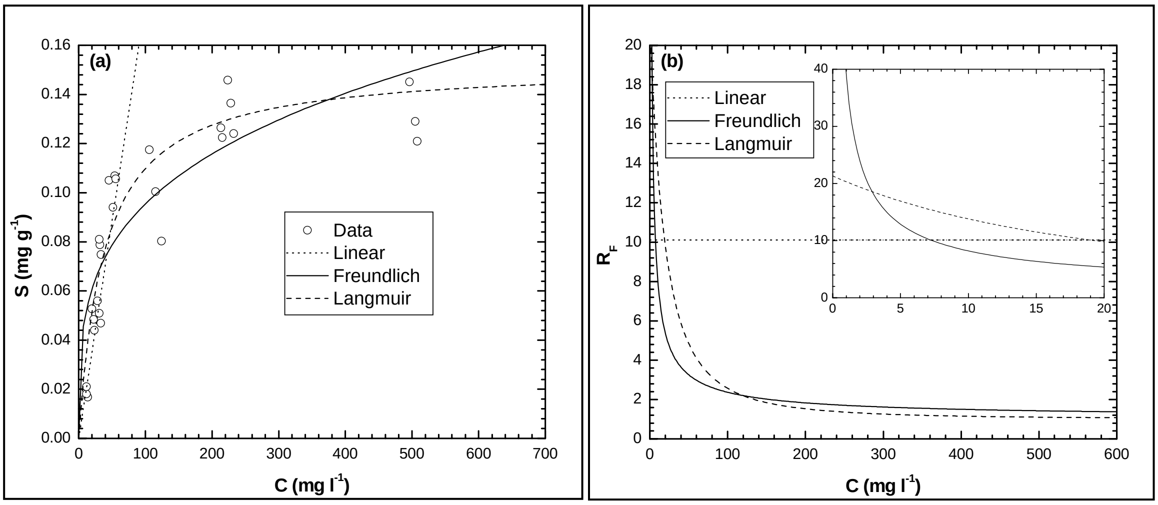

Figure 1 – (a) Sorption isotherms for the case of surfactant sorption (Weber et al., 1996); (b) Resulting retardation factors

Physical paradoxes

The first source of numerical difficulty is the magnitude of the isotherm slope, which varies with concentration for the non-linear case. Depending on the isotherm parameters and on the range of concentrations, the isotherm can be too steep, and the resulting transport problem too stiff for traditional solution approaches. In some cases, such as in the Freundlich isotherm case for $0 < N < 1$, the slope of the isotherm given by equation (8) tends to infinite for small concentrations and is not defined at $C = 0$ (see Fig. 1b), characterizing a numerical singularity in the governing equation at $C = 0$. From the mathematical standpoint, this singularity causes the formation of traveling waves and the instantaneous shrinking of the solution support, as discussed in the previous section. From the physical standpoint, a couple of ensuing paradoxes may affect the ability of the Freundlich isotherm to conceptually model groundwater transport.

The first physical paradox caused by the infinite slope of the Freundlich isotherm ($0 < N < 1$) at zero concentration is that, if that in fact happened the porous medium would behave as having a sorption capacity tending to infinity (or an infinitely high affinity for the solute) as the solute concentration decreased towards zero, and thus would bind the solute so strongly that minute amounts of solute would never be released from the porous medium even after being equilibrated with clean water for very large time scales. Obviously this situation is antagonistic to the initial assumption of thermodynamic equilibrium of the isotherm, either in a batch system or in groundwater transport.

The second physical paradox originated from the infinite sorption capacity of the Freundlich isotherm at zero concentration appears when a contaminant front infiltrates in a clean aquifer. In this dynamic situation, the instantaneous local equilibrium assumption would be conceptually flawed at points located at the leading edge of the front (close to $C = 0$), and other transport processes (such as boundary layer effects, or film diffusion) would impose a mass transfer limitation to sorption. Hence, the sorption phenomenon would be better described by a non-equilibrium model. These physical paradoxes are conceptual limitations of the Freundlich isotherm model when describing very low concentrations, which can typically occur when modeling groundwater transport in environmental applications.

Numerical difficulties

A basic requirement for mass conservation of the numerical solution is that the approach for calculating the isotherm slope (or the retardation factor) in the numerical solution of the transport equation needs to preserve equivalence between the original and the discretized (weak) versions of the partial differential equation (PDE), as. Given that the following equivalence for the mass-term of Equation (6a) holds for any point (for constant ρ_b and n):

$$R(C)\frac{\partial C}{\partial t} = \frac{\partial T}{\partial t} \qquad (10),$$

where T is the total concentration given by:

$$T = C + \frac{\rho_b}{n} S \qquad (11),$$

then the same type of equivalence must also hold for the weak version of the PDE. The method here presented is directly derived from the application of the standard Galerkin method onto the 'concentration-based' formulation, equation (6). Table 1 shows two approaches to handle the mass-term of the transport equation in the concentration-based formulation: the 'traditional' and the 'non-traditional' approaches, following the nomenclature of Rathfelder and Abriola (1994) for the Richards equation. The rows of the column show, in different notations, the equivalence that must be preserved in the finite element version of the mass term. The components a_{Qi}, b_{Qi}, c_{Qi}, a_{Ei}, b_{Ei}, c_{Ei} ($i = 1,\ldots,M+1$, where M is the number of elements of the finite element mesh) are respectively the lower, main and upper diagonals of the mass-matrices $[Q_T]$ and $[Q_N]$ and $[E]$, whereas $b_{Qi}{}^{L}$ are the components of the main diagonals of the lumped mass matrices for each approach. The symbol ^ denotes the finite element expansion, m+1 is the new iteration step of the current time step, and k is the previous time step.

Table 1 – Finite element approaches for the mass (accumulation) term

a) Traditional	**b) Non-traditional**
$\frac{\partial \hat{T}}{\partial t} \cong \frac{\partial T}{\partial t} = R(C)\frac{\partial C}{\partial t} \cong \hat{R}(\hat{C})\frac{\partial \hat{C}}{\partial t}$ $\sum_{j=1}^{M}\frac{dT_j}{dt}N_j = \left(\sum_{l=1}^{M}R_l(C_l)N_l\right)\left(\sum_{j=1}^{M}\frac{dC_j}{dt}N_j\right)$	$\frac{\partial \hat{T}}{\partial t} \cong \frac{\partial T}{\partial t} = R(C)\frac{\partial C}{\partial t} \cong \overbrace{R(\hat{C})\frac{\partial C}{\partial t}}$ $\sum_{j=1}^{M}\frac{dT_j}{dt}N_j = \sum_{j=1}^{M}R_j(C_j)\frac{dC_j}{dt}N_j$
$(1/\Delta t)[E]\{\Delta T_i\}^{m+1} = (1/\Delta t)[Q_T]\{\Delta C_i\}^{m+1}$	$(1/\Delta t)[E]\{\Delta T_i\}^{m+1} = (1/\Delta t)[Q_N]\{\Delta C_i\}^{m+1}$
$[Q_T]$ $a_{Qi} = \frac{1}{6}\Delta x_{i-1}\left(\frac{R_{i-1}+R_i}{2}\right)$ $b_{Qi} = \frac{1}{6}\left[\Delta x_{i-1}\frac{R_{i-1}}{2} + 3\left(\frac{\Delta x_{i-1}+\Delta x_i}{2}\right)R_i + \Delta x_i\frac{R_{i+1}}{2}\right]$ $c_{Qi} = \frac{1}{6}\Delta x_i\left(\frac{R_i+R_{i+1}}{2}\right)$	$[Q_N]$ $a_{Qi} = \frac{1}{6}\Delta x_{i-1}R_{i-1}$ $b_{Qi} = \frac{1}{6}\left[4\left(\frac{\Delta x_{i-1}+\Delta x_i}{2}\right)R_i\right]$ $c_{Qi} = \frac{1}{6}\Delta x_i R_{i+1}$
$b_{Qi}^{L} = \frac{1}{6}\left[\Delta x_{i-1}R_{i-1} + 4\left(\frac{\Delta x_{i-1}+\Delta x_i}{2}\right)R_i + \Delta x_i R_{i+1}\right]$	$b_{Qi}^{L} = \left(\frac{\Delta x_{i-1}+\Delta x_i}{2}\right)R_i$

$$a_{Ei} = \frac{\Delta x_{i-1}}{6}\;;\qquad b_{Ei} = \frac{\Delta x_{i-1}+\Delta x_i}{3}\;;\qquad c_{Ei} = \frac{\Delta x_i}{6}$$

$$\{\Delta C\}^{m+1} = \{C\}^{m+1} - \{C\}^{k}$$

$$\{\Delta T\}^{m+1} = \{T\}^{m+1} - \{T\}^{k}$$

As shown in the first row of Table 1, the basic difference between the two approaches is that, in the traditional approach, the retardation factor is also expanded in terms of the basis functions separately from the concentration field, whereas the non-traditional approach employs a single basis function to approximate the chain rule expansion of the storage term (Abriola and Rathfelder, 1993).

On the finite element solution of the transport equation in the concentration-based formulation, equivalence (10) only holds and contaminant mass is conserved if two conditions are simultaneously met: (i) an appropriate finite element expansion is used for the term on the left hand side, and (ii) the non-linear slope of the isotherm ($\partial S/\partial C$) is calculated in an appropriate way, as it will be presented below.

Equivalence (10) is generally not be preserved on the traditional FEM expansion for the mass term of equation (6a) when it is non-linear. This is especially true in the case of the Freundlich isotherm, where even a 'distributed chord slope' scheme – similarly to the one defined by Rathfelder (1994), would not work. The basic reason for that is because, in the traditional finite element expansion, C_i at a node i would be multiplying $R(C_{i-1})$, $R(C_i)$, and $R(C_{i+1})$ on the discretized equations. For instance, from Table 1 the diagonal term of the finite element mass matrix in the traditional approach would be (for a fixed Δx):

$$b_{Qi}C_i = \frac{\Delta x}{12\Delta t}\left[R(C_{i-1}) + 6R(C_i) + R(C_{i+1})\right]C_i \qquad (12).$$

As in the example of a contamination event of an initially clean aquifer, the case where $C_i > 0$ and $C_{i+1} = 0$ would happen. If in this case Freundlich sorption happens, then $R(C_{i+1})$ would tend to infinite and the product $C_i \cdot R(C_{i+1})$ would be too large to be represented in finite computer precision. Some authors have circumvented this problem by imposing an arbitrary numerical 'cap' on the isotherm slope, thus limiting its numerical value (Jaekel et al., 1996; Jaekel and Vereecken, 2002; van der Zee, 1990; and Vereecken et al., 2002). However, as shown below, this cap does not adequately represent an initially clean aquifer and produces spurious results that are dependent on its value. Thus, the non-traditional approach is required as one of the conditions for mass-balance preservation in the concentration-based formulation for the transport equation.

The scheme of calculating the slope of the non-linear isotherm also has an important influence on the preservation of equivalence (10) and on the mass balance of the finite element solution. Still today, some widely used commercial codes (Šimunek et al., 1999; Voss and Provost, 2002) employ an analytical derivative to calculate the isotherm slope in Equation (6b), either in conjunction with a 'cap' on the slope (Šimunek et al., 1999) or with a predictor-corrector scheme that partially linearizes the non-linear coefficient and 'caps' the non-linear part (Voss and Provost, 2002). However, in the case of non-linear isotherms, if the required non-traditional approach is used on the mass-term, the use of a finite element chord slope scheme (*fecs*) for the numerical evaluation of the isotherm slope, rather than the more commonly used analytical slope, is required to preserve the equivalence of the mass term from the original PDE on the discretized finite element form. The *fecs* scheme can be used in conjunction with a Picard iteration scheme to update the non-linear coefficient:

$$\left.\frac{\partial S}{\partial C}\right|_i^m = \frac{S_i^m - S_i^k}{C_i^m - C_i^k} \qquad (11)$$

where the values of C_i^m and S_i^m are lagged one iteration step to resolve the non-linearity.

In summary, two major numerical difficulties are found in the finite element solution of the transport equation with non-linear local equilibrium sorption, and most pronounced in the Freundlich case: (i) the steep slope or the singularity at low concentrations and the associated need for a ‘numerical cap’ on the retardation factor when a traditional approach for the mass-term of the transport equation is used; (ii) the expansion approach for the nonlinear mass term the calculation scheme for the slope of the non-linear isotherm, and subsequent influence in the global mass-balance of the solution. The following section shows results that illustrate these numerical difficulties and presents numerical schemes that can resolve them.

RESULTS AND DISCUSSION

Effect of Finite Element Approach on Transport Predictions

Several numerical simulations were performed in order to show the effect of the solution approach on model predictions for the transport equation with non-linear sorption. Initially, the effect of the C_{cap} on breakthrough curves and concentration profiles were compared for the traditional and non-traditional approach for the Freundlich case. Then, the effect of the scheme of calculation of the non-linear slope on the mass-balance was assessed for the non-traditional approach. The following sorption and transport parameters were used, taken from one of the examples from Weber et al. (1996): Length of the column: L = 12 cm; Bulk density of the porous medium: ρ_b = 1.671 g cm^{-3}; Porosity: n = 0.3; Pore velocity: v = 9.76 cm h^{-1}; Injection concentration: C_0 = 100 mg L^{-1}; Duration of the pulse: 3 pore volumes; Dispersion coefficient: D = 0.5856 cm^{2}h^{-1}; Freundlich parameters: K_F = 0.0264 mg g^{-1}(L mg^{-1})^N; N = 0.279; Langmuir parameters: $S_{\max}$ = 0.152 mg g^{-1}; ω = 0.026 L mg^{-1}.

In order to avoid the singularity of the Freundlich isotherm at C = 0, a numerical ‘cap’ on the minimum concentration for which the retardation factor would be calculated (C_{cap}) was selected, as explained on the previous section. At concentrations below C_{cap}, R was kept constant at the value of $R(C_{\mathrm{cap}})$. Figure 2 shows the effect on the breakthrough curve of changing the cap for a domain with 1500 elements ($Pe_{Grid} = 0.175$). For the traditional approach (Fig. 2a), when $C_{\mathrm{cap}} < 0.05$ mg L^{-1}, the breakthrough curves move even further to the right, and there is no value for C_{cap} that provides converged results. The cause of this problematic behavior was explained in the previous section. Figure 2b shows that in the non-traditional formulation below a certain reasonable value of C_{cap}, the cap is irrelevant, since at the nodes upstream of the solute front were the retardation factor is bounded by $R(C_{\mathrm{cap}})$, the concentration C_i that multiplies $R(C_{\mathrm{cap}})$ in the algebraic system is so low that their product is negligible and the solution is not affected.

Figure 3a shows the profiles after 1, 3, and 3.5 pore volumes for the traditional case with $C_{\mathrm{cap}} = 0.05$ mg L^{-1}. The distributed nature of the retardation factor featured in this formulation and the unrealistic yet necessary cap caused the front almost not to infiltrate into the porous medium. Figure 3b illustrates how the profiles have infiltrated more in the porous medium after 1, 3, and 3.5 pore volumes for the non-traditional case when $C_{\mathrm{cap}} = 10^{-7}$ mg L^{-1}, than for the traditional case. The results shown here confirm that it is not possible to find a finite element solution for the Freundlich problem using the traditional expansion of the mass term due to the singularity at $C = 0$ and to the distributed nature of the coefficients of the matrix $[Q_{\mathrm{T}}]$, as explained above. They also show that, in the case of a contamination front infiltrating in a clean aquifer, the traditional approach may provide non-conservative results for lower values of C_{cap}, in the sense that a groundwater contamination front would appear to reach the receptor much later than what it indeed does.

For the non-traditional formulation, a convergence analysis was performed for various grid refinements, given by: $Pe_{Grid} = 0.0875$, 0.175, 0.875, and 1.75 (or 3000, 1500, 300 and 150 elements respectively), confirming that the results presented here for 1500 elements in the non-traditional case were very well converged. A variable, self-adjusting, time step was employed, based on the successful convergence of a Picard iterative procedure for the non-linear coefficient.

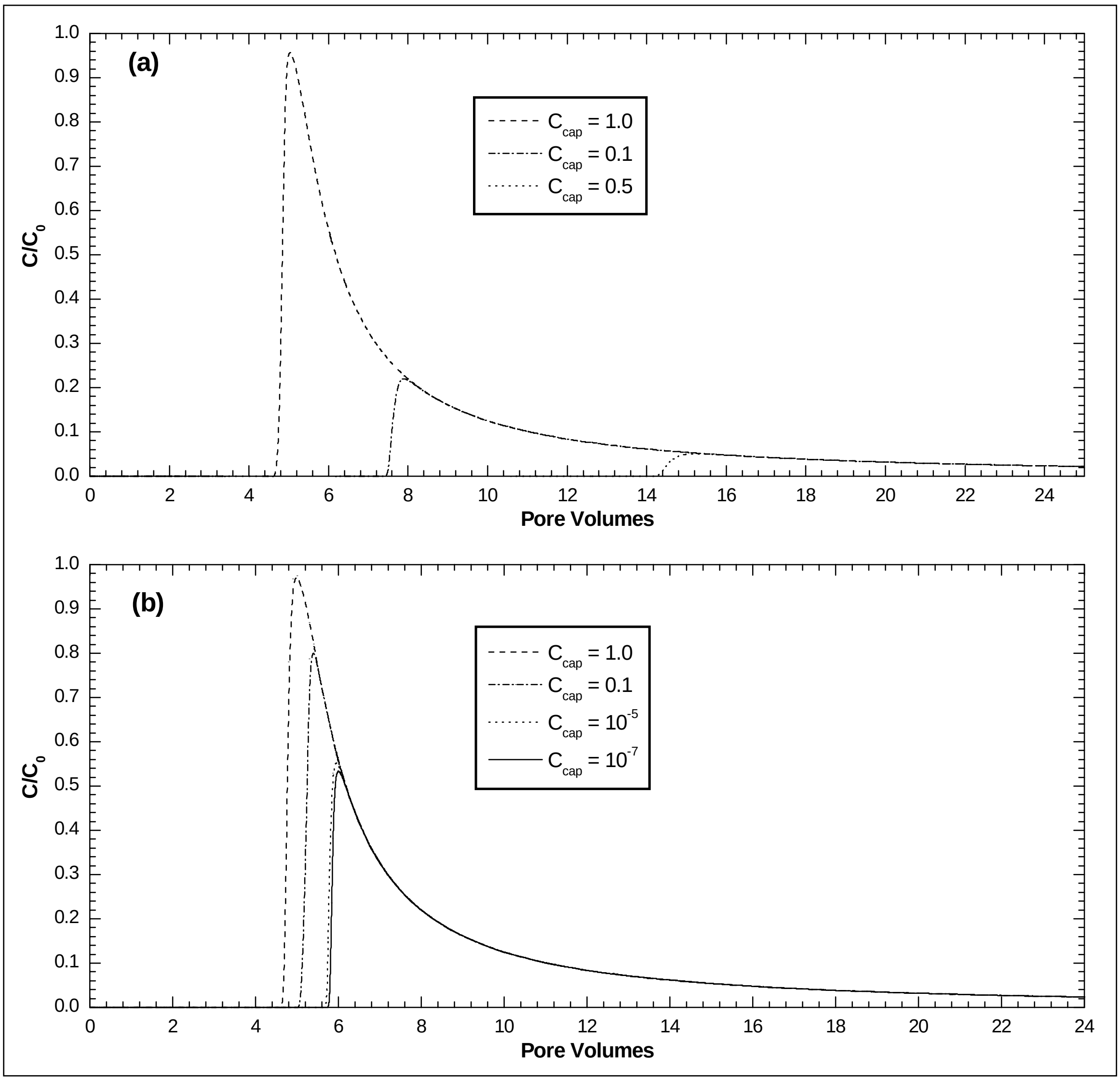

Figure 2 – Effect of varying C_{cap} on the breakthrough curves.

(a) Traditional formulation; (b) Non-Traditional formulation.

The effect of the scheme of calculation of the isotherm slope (analytical vs. *fecs*) was then evaluated for the non-traditional approach of expansion of the mass term in the concentration-based formulation. Both Langmuir and Freundlich cases were analyzed and the results for Freundlich are shown here. The mass balance in the traditional expansion was inadequate as a consequence of the inability of the model to describe the highly non-linear sorption cases, thus the mass balance results for this case are not shown here. The 'analytical slope' is calculated as the analytical derivative of $\partial S/\partial C$ (Eqns. 8 and 9) at each node, while the finite element chord slope (*fecs*) scheme uses the expression given by Equation (11). The *fecs* scheme maintains the original consistency of the mass term from the original PDE (Eqn. 10) on the discretized finite element form when the non-traditional approach is used, as explained above. The cumulative mass balance error at time *t* is given by Rathfelder and Abriola (1994):

$$TMPERC = \left(1 - \frac{TMSTOR}{TMFLUXB}\right) \times 100\% \qquad (12)$$

where *TMSTOR*(*t*) is the total mass stored in the domain at time *t*, and *TMFLUXB*(*t*) is the cumulative mass that has flown across the boundaries in the interval [0, *t*].

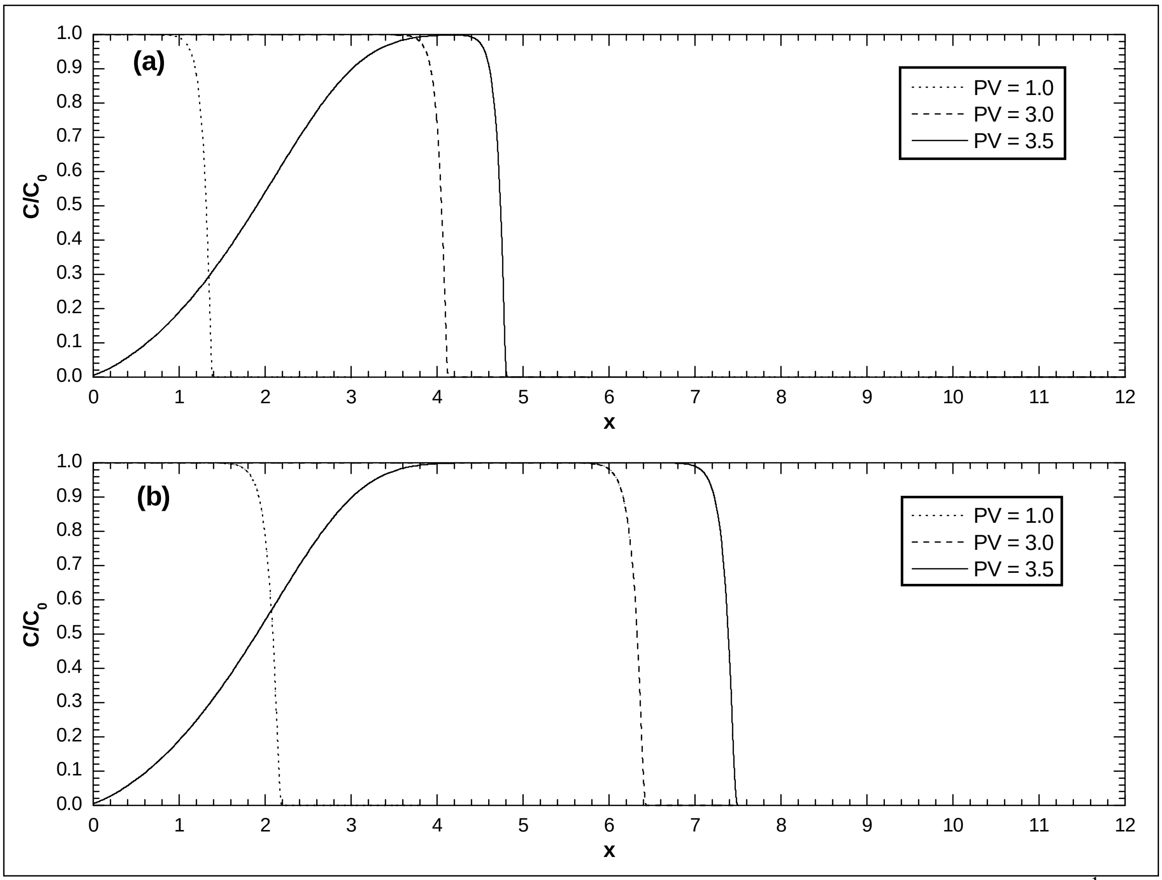

Figure 3 – Concentration profiles: (a) Traditional formulation: $C_{\mathrm{cap}} = 0.05$ mg L^{-1}; (b) Non-Traditional formulation: $C_{\mathrm{cap}} = 10^{-7}$ mg L^{-1}.

Figure 4 shows the effect of the calculation scheme for the Freundlich slope on the cumulative mass balance error. Both cases were simulated with 300 elements ($Pe_{Grid} = 0.875$) and a $C_{\mathrm{cap}} = 10^{-7}$ mg L^{-1}. The analytical slope scheme resulted in a mass balance error much greater than the finite element chord slope scheme, as can be noticed on figure 4. The *fecs* scheme presented negligible mass balance errors (in general lesser than 0.02%). Therefore, it is recommended that a non-traditional approach be used in conjunction with the *fecs* scheme for the finite element solution of the transport equation in the concentration-based formulation.

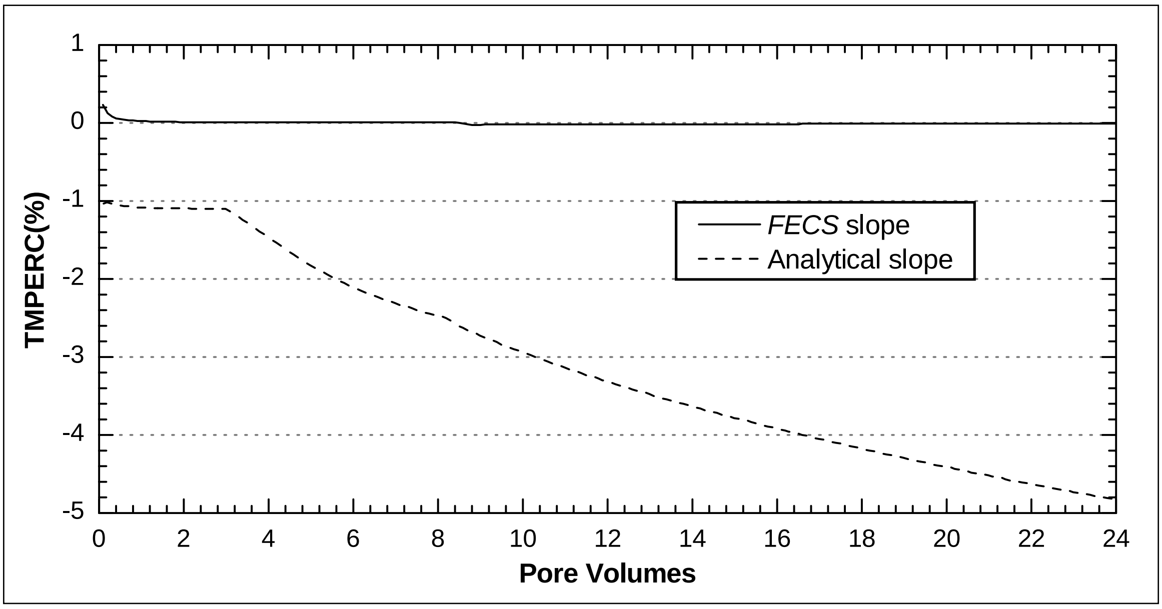

Figure 4 – Freundlich mass balance. Analytical slope vs. *fecs* formulation for the isotherm slope.

Effect of Isotherm Model Selection on Transport Predictions

The mass-conservative finite-element model developed in the present study was used to obtain converged predictions for breakthrough curves (BTCs) after the injection of 1 pore volume of surfactant at the concentration of 100 mg/l, followed by flushing with clean water. The same input parameters used by Weber et al. (1996) were employed (as reported in the previous section) with 300 elements in the domain. As Figure 1a shows, both non-linear isotherms fit well the data, and the linear isotherm fits roughly the data within the concentration range of the numerical simulations.

The analysis of the BTCs obtained in the present study (Fig. 5) shows the differences between the predictions for each isotherm. First, the non-linear isotherm fronts arrive before the linear isotherm. Figure 1b shows that a liberally defined "average" retardation factor for the range $0 < C < 100$ mg/l would be greater for the linear isotherm, followed by the Langmuir isotherm and the Freundlich isotherm, respectively. This fact could explain the order of arrival of the front, although at this point this type of analysis should only be carefully considered as a rough estimate, due to the non-linear and complex behavior of the transport equation.

Although the present results show sizable differences between the different isotherm transport predictions (despite the batch isotherm fits not being so much different from each other), a clear discrepancy is found between the current predictions for the Freundlich BTC and the predictions obtained by Weber et al. (1996) (also shown in Fig. 5). Although the solution method of Weber et al. (1996) was not clearly reported, their BTC results are very similar to those of an incorrect use of a 'cap' on the isotherm slope as observed in the previous section. In fact, the use of an analytical derivative for calculating the slope, associated with a 'cap' was a common practice at that time

(Šimunek et al., 1999; Voss and Provost, 2002), and suggest a plausible reason for the discrepant results from Weber et al. (1996).

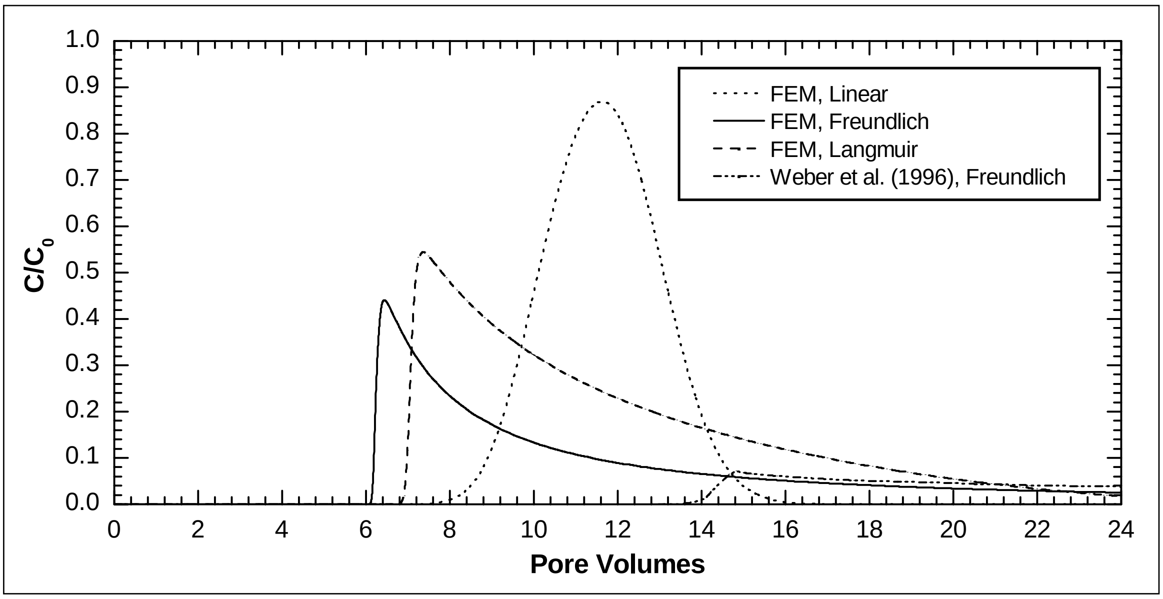

Figure 5 – Comparison of present breakthrough curves with published result from (Weber et al., 1996)

The present results also disagree with the generality of the conclusion from Weber et al. (1996), who claimed that the most significant difference between the linear and Freundlich predictions was the "slower rate of travel of the center of mass when the Freundlich model was employed", and that this was reflective of the model's ability to account for the higher sorption capacities observed at lower solution-phase concentrations. In fact, the higher retardation of the Freundlich isotherm at very small concentrations causes the front to be steeper in this case, but does not cause it to be more retarded than in the two other cases. In the present study, the tailing of the Freundlich case is much greater than the linear and Langmuir cases, which could be explained by the high sorption capacities at small concentrations as the contaminant de-sorbs from the porous medium.

CONCLUSION

Local equilibrium isotherms have been frequently used in the groundwater literature to model sorption phenomena occurring at the interface between groundwater and the solid porous matrix. However, non-linear isotherms pose interesting numerical difficulties in the solution of the transport equation, which are even more pronounced in the case of the Freundlich isotherm, whose slope presents a numerical singularity at zero concentration, as is common upstream of contamination fronts. This singularity leads to very large sorption capacities close to zero concentration, which causes thermodynamic and physical conceptual paradoxes when this isotherm is used in flowing groundwater systems.

The present study showed that a non-traditional expansion of the mass-term of the transport equation in the concentration-based formulation and the numerical evaluation of the non-linear slope of the isotherm using a finite element chord slope scheme (*fecs*) are required for the mass-conservative numerical solution of the transport equation with non-linear equilibrium sorption, since it preserves the equivalence of the mass-term on the weak (discretized) formulation. Numerical approaches that employ the traditional expansion or an analytical slope evaluation of the isotherm slope not only incur in large mass-balance errors, but often require the use of an unrealistic numerical limiter ('cap') for the retardation factor, which can result in spurious results in the numerical solution.

The re-assessment of the transport predictions presented by (Weber et al., 1996) using the present model and three different isotherms fitted to the same set of experimental data shows that the Freundlich isotherm in fact breaks through before the Langmuir and Linear isotherms, probably because the smaller 'average' retardation factor in the concentration range of the injected pulse. Hence, the present results challenge the generality of the conclusion presented by Weber et al. (1996).

Despite the numerical difficulties, the applicability of nonlinear isotherms depends on their capacity to describe real batch sorption data over wider ranges of concentrations than other models. The validity of employing a nonlinear isotherm to model groundwater transport in real systems can only be tested by comparing transport simulations based on isotherm parameters obtained from batch sorption experiments with real transport data. Towards that end, this study highlighted the importance of obtaining an accurate solution of the transport equation with non-linear sorption. An appropriate numerical solution that conserves mass and that maintains the equivalence between the original PDE and its weak formulation is of utmost importance. As identified in the present study, the numerical solution of the transport equation for a contaminant that undergoes nonlinear sorption can also pose numerical difficulties, and a non-traditional approach associated to a finite element chord slope iterative scheme (*fecs*) must be employed to achieve mass-conservative finite-element solutions to the transport equation in the concentration-based formulation.

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