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NUMERICAL SOLUTIONS FOR NONEQUILIBRIUM SOLUTE TRANSPORT WITH FIRST-ORDER DECAY AND ZERO-ORDER PRODUCTION

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Abstract. Solute transport in the subsurface is often considered to be a nonequilibrium process. Nonequilibrium during transport of solutes in porous medium has been categorized as either transport-related or sorption-related. For steady state flow in a homogeneous soil and assuming a linear sorption process, we will consider advection-diffusion adsorption equations. In this paper, numerical methods are considered for the mathematical model for steady state flow in a homogeneous soil with a linear sorption process. The modified upwind finite difference method is adopted to approximate the concentration in mobile regions and immobile regions. Optimal order l^2- error estimate is derived. Numerical results are supplied to justify the theoretical work.

Key words. Solute transport, error estimate, modified upwind finite difference.

1. Introduction

Solute transport in the subsurface is often considered to be a nonequilibrium process. Nonequilibrium during transport of solutes in porous medium has been categorized as either transport-related or sorption-related. Transport nonequilibrium (also called physical nonequilibrium) is caused by slow diffusion between mobile and immobile water regions. These regions are commonly observed in aggregated soils [8, 12] or under unsaturated flow conditions [2, 13, 14, 15], or in layered or otherwise heterogeneous groundwater systems. Sorption-related nonequilibrium results from either slow intrasorbent diffusion [1] or slow chemical interaction [7]. In most of these models, the soil matrix is conceptually divided into two types of sites; sorption is assumed to be instantaneous for one type and rate-limited for the other type.

Solute transfer between immobile/mobile water regions or instantaneous/ rate-limited sorption sites is commonly described by a first-order rate expression or by Fica's law if the geometry of the porous matrix can be specified. Models that are based on well-defined geometry are difficult to apply to actual field situations, they require information about the geometry of the structural units that are rarely available [6]. Hence, the first-order rate formulation has been extensively used to model underground contaminant transport. We start with a brief outline of two-site nonequilibrium models as well as the two-region physical nonequilibrium models which were given in [16]. General solutions are derived for the volume-averaged solute concentration using Laplace transforms in [16].

Model

(1) Two-site Nonequilibrium Transport Model

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The two-site sorption model makes a distinction between type-1 (equilibrium) and type-2 (first-order kinetic) sorption sites [9] and is given by

$$(1)\qquad \begin{aligned}(1+\frac{f\rho k}{\theta})\frac{\partial c}{\partial t} &= D\frac{\partial^2 c}{\partial x^2}-v\frac{\partial c}{\partial x}-\frac{\alpha\rho}{\theta}[(1-f)kc-s_k]-\mu_l c\\ &- \frac{f\rho\mu_{s,e}c}{\theta}+\gamma_l(x)+\frac{f\rho\gamma_{s,e}(x)}{\theta},\end{aligned}$$

$$(2)\qquad \frac{\partial s_k}{\partial t}=\alpha[(1-f)kc-s_k]-\mu_{s,k}s_k+(1-f)\gamma_{s,k}(x).$$

where c is the volume-averaged concentration of the liquid phase; s is the concentration of the sorbed phase; D is the dispersion coefficient; θ is the volumetric water content; $v = q/\theta$ is the average pore water velocity in which q is the volumetric water flux density; ρ is the bulk density; μ_l and μ_s are first-order decay coefficients for degradation in the liquid and sorbed phases, respectively; γ_l and γ_s are zero-order production terms for the liquid and sorbed phase, respectively; k is a distribution coefficient for linear sorption; α is a first-order kinetic rate coefficient; f is the fraction of exchange sites assumed to be at equilibrium; x is distance; t is time; and the subscripts e and k refer to equilibrium and kinetic sorption sites, respectively.

(2) Two-Region Nonequilibrium Transport Model

The two-region transport model assumes that the liquid phase can be partitioned into mobile (flowing) and immobile (stagnant) regions and that solute exchange between the two liquid regions can be modeled as a first-order process. The model is given by

$$(3)\qquad \begin{aligned}(\theta_m+f\rho k)\frac{\partial c_m}{\partial t} &= \theta_m D_m\frac{\partial^2 c_m}{\partial x^2}-q\frac{\partial c_m}{\partial x}-\alpha(c_m-c_{im})\\ &- (\theta_m\mu_{l,m}+f\rho k\mu_{s,m})c_m+\theta_m\gamma_{l,m}(x)+f\rho\gamma_{s,m}(x),\end{aligned}$$

$$(4)\qquad \begin{aligned}(\theta_{im}+(1-f)\rho k)\frac{\partial c_{im}}{\partial t} &= \alpha(c_m-c_{im})-(\theta_{im}\mu_{l,im}+(1-f)\rho k\mu_{s,im})c_{im}\\ &\quad +\theta_{im}\gamma_{l,im}(x)+(1-f)\rho\gamma_{s,im}(x).\end{aligned}$$

where the subscripts m and im refer to mobile and immobile liquid regions, respectively; the subscripts l and s refer to the liquid and sorbed phases, respectively; f represents the fraction of sorption sites that equilibrates with the mobile liquid phase and α is a first-order mass transfer coefficient governing the rate of solute exchange between mobile and immobile liquid regions. Note that θ is equal to $\theta_m + \theta_{im}$.

If we employ dimensionless parameters listed in Table 1, equations (1), (2) and (3), (4) reduce to the same dimensionless form. Dimensionless equations of the nonequilibrium model for the case of linear sorption are given by

$$(5)\qquad \beta R\frac{\partial C_1}{\partial T}=\frac{1}{P}\frac{\partial^2 C_1}{\partial X^2}-\frac{\partial C_1}{\partial X}-\omega(C_1-C_2)-\mu_1 C_1+\gamma_1(X),$$

$$(6)\qquad (1-\beta)R\frac{\partial C_2}{\partial T}=\omega(C_1-C_2)-\mu_2 C_2+\gamma_2(X).$$

TABLE 1. Dimensionless Parameters for the Two-Site and Two-Region Transport Models

parameter	two-site	two-region
T	vt/L	vt/L
X	x/L	x/L
P	vL/D	$v_m\mathrm{L}/D_m$
R	$1+\rho\mathrm{k}/\theta$	$1+\rho\mathrm{k}/\theta$
β	$\frac{\theta+f\rho k}{\theta+\rho k}$	$\frac{\theta_m+f\rho k}{\theta+k\rho}$
ω	$\frac{\alpha(1-\beta)RL}{v}$	$\frac{\alpha L}{\theta v}$
C_1	$\frac{c}{c_0}$	$\frac{c_m}{c_0}$
C_2	$\frac{s_k}{(1-f)kc_0}$	$\frac{c_{im}}{c_0}$
μ_1	$\frac{(\theta\mu_l+f\rho k\mu_{s,e})L}{\theta v}$	$\frac{(\theta_m\mu_{l,m}+f\rho k\mu_{s,m})L}{\theta v}$
μ_2	$\frac{(1-f)\rho k\mu_{s,k}L}{\theta v}$	$\frac{(\theta_{im}\mu_{l,im}+(1-f)\rho k\mu_{s,im})L}{\theta v}$
γ_1	$\frac{L(\theta\gamma_l+f\rho\gamma_{s,e})}{\theta v c_0}$	$\frac{L(\theta_m\gamma_{l,m}+f\rho\gamma_{s,m})}{\theta v c_0}$
γ_2	$\frac{L(1-f)\rho\gamma_{s,k}}{\theta v c_0}$	$\frac{L(\theta_{im}\gamma_{l,im}+(1-f)\rho\gamma_{s,im})}{\theta v c_0}$

Here c_0 and L represent characteristic concentrations and lengths, respectively.

where C_1 is the reduced volume-averaged solute concentration, C_2 is the reduced kinetically adsorbed concentration, μ is a first-order decay coefficient, γ is a zero-order production coefficient, X and T are space and time variables, respectively; β, R, P and ω are adjusted model parameters and subscripts 1 and 2 on μ and γ refer to equilibrium and nonequilibrium sites, respectively. We shall assume that ω and μ cannot be negative. Notice that zero-order production terms in (5) are functions of position X, but that first-order rate coefficients are assumed to be constant. Subscripts 1 and 2 refer to mobile and immobile regions if dimensionless transport equations are interpreted in terms of the two-region model.

These dimensionless transport equations given by (5) (6) will be solved for the following general initial and boundary conditions:

$$C_1(X,0) = C_2(X,0) = C_i(X), \tag{7}$$

$$\left(-\frac{\delta}{P}\frac{\partial C_1}{\partial X} + C_1\right)\Big|_{X=0} = C_0(T), \tag{8}$$

with $\delta = 0$ for a first-type and $\delta = 1$ for a third-type boundary condition and

$$\frac{\partial C_1}{\partial X}(\infty, T) = 0, \tag{9}$$

where C_i is the initial concentration and C_0 is the boundary concentration.

The organization of the paper is as follows. In section 2, the modified upwind difference methods is proposed to the dimensionless mathematical model for steady state flow in a homogeneous soil with a linear sorption process. Optimal order estimate in l^2- norm is derived. In section 3, numerical results were presented for the nonequilubrium transport model which was given in [16].

2. The modified upwind finite difference method

There have been many numerical methods for miscible displacement in porous media. In [5] the finite difference method is proposed combining with the method of characteristic method for convection-dominated problems in porous media. An alternating direction method combined with a modified method of characteristic is presented in [4] for miscible displacement influenced by mobile water and immobile water. Yi-rang Yuan [17] formulated a modified upwind finite difference procedure for compressible two-phase displacement problems. The modified upwind finite difference method is efficient to treat the equation with significant convection and has the second-order accuracy in space variable.

We assume that coefficients satisfy:

$$0 < a_* \le a(x) \le a^*, \quad 0 < b_* \le b(x) \le b^*, \quad 0 < D_* \le D(x) \le D^*,$$

where $a_*, a^*, b_*, b^*, D_*, D^*$ are positive constants.

We also assume that the solution c_1, c_2 of (5) and (6) satisfy:

(10)
$$c_1, c_2 \in W^{1,\infty} \bigcap L^\infty(W^{4,\infty}), \frac{\partial c_1}{\partial t}, \frac{\partial c_2}{\partial t} \in L^\infty(W^{1,\infty}), \frac{\partial^2 c_1}{\partial t^2}, \frac{\partial^2 c_2}{\partial t^2} \in L^\infty(W^{1,\infty}).$$

For convenience, we introduce new parameters:

$$u = 1, \ D = 1/P, \ a = \beta R \ b = (1-\beta)R.$$

For the sake of simplicity, denote the bounded domain $\Omega = [0,1]$, the space step $h = \frac{1}{N}$, code $x_i = ih$, $i = 0, 1...N$, the time step $t^n = n\Delta t$, and $c_i^n = c(x_i, t^n)$, $w_{ij}^n = w(x_{ij}, t^n)$.

Let δ_x, δ_y and $\delta_{\bar{x}}$, $\delta_{\bar{y}}$ stand for standard backward difference respectively.

Define

$$D_{i+\frac{1}{2},j} = \frac{D_{i+1,j} + D_{i,j}}{2}, D_{i-\frac{1}{2},j} = \frac{D_{i-1,j} + D_{i,j}}{2}.$$

Similarly, we can define $D_{i,j+\frac{1}{2}}, D_{i,j-\frac{1}{2}}$.

Now, assume $\{C_{1,ij}^n, C_{2,ij}^n\}$ are known. Then the modified upwind finite difference method for (5) (6) is given by: finding that $\{C_{1,ij}^{n+1}, C_{2,ij}^{n+1}\}$, for $1 \le i, j \le N-1$ satisfying

(11)
$$\begin{aligned} & a_{ij}\frac{C_{1,ij}^{n+1} - C_{1,ij}^n}{\Delta t} + b_{ij}\frac{C_{2,ij}^{n+1} - C_{2,ij}^n}{\Delta t} + \delta_{U^{n+1},x} C_{1,ij}^{n+1} + \delta_{W^{n+1},y} C_{1,ij}^{n+1} \\ & -\Big\{\Big(1 + \tfrac{h}{2}\tfrac{|U_{ij}^{n+1}|}{D_{ij}}\Big)^{-1} \delta_{\bar{x}}(D\delta_x C_{ij}^{n+1}) + \Big(1 + \tfrac{h}{2}\tfrac{|W_{ij}^{n+1}|}{D_{ij}}\Big)^{-1} \delta_{\bar{y}}(D\delta_y C_{ij}^{n+1})\Big\} \\ & +\mu_{1,ij} C_{1,ij}^{n+1} + \mu_{2,ij} C_{2,ij}^{n+1} = \gamma_{1,ij} + \gamma_{2,ij}, \end{aligned}$$

(12)
$$b_{ij}\frac{C_{2,ij}^{n+1} - C_{2,ij}^n}{\Delta t} = \omega(C_{1,ij}^{n+1} - C_{2,ij}^{n+1}) - \mu_{2,ij} C_{2,ij}^{n+1} + \gamma_{2,ij},$$

where

$$\delta_{U^n,x} C_{1,ij}^n = U_{ij}^n \Big\{ H(U_{ij}^n) D_{ij}^{-1} D_{i-\frac{1}{2},j} \delta_{\bar{x}} C_{ij}^n + \Big(1 - H(U_{ij}^n)\Big) D_{ij}^{-1} D_{i+\frac{1}{2},j} \delta_x C_{ij}^n \Big\},$$

$$\delta_{W^n,y}C^n_{1,ij} = W^n_{ij}\Big\{H(W^n_{ij})D^{-1}_{ij}D_{i,j-\frac{1}{2}}\delta_{\bar{y}}C^n_{ij} + \Big(1 - H(W^n_{ij})\Big)D^{-1}_{ij}D_{i,j+\frac{1}{2}}\delta_y C^n_{ij}\Big\},$$

$$H(z) = \begin{cases} 1, & z \geq 0, \\ 0, & z < 0. \end{cases}$$

and initial values are given by:

$$C^0_{1,ij} = c_{1,0}(x_{ij}), \quad C^0_{2,ij} = c_{2,0}(x_{ij}), \quad 0 \leq i,j \leq N.$$

3. Convergence Analysis

Let $\zeta = c_1 - C_1$ and $\xi = c_2 - C_2$, where c_1, c_2 are the solutions of (5) (6) and C_1, C_2 are numerical solutions of difference scheme (11) (12) respectively. Then we define the inner product and norm in discrete space $l^2(\Omega)$.

$$(f^n, g^n) = \sum_{i,j=1}^{N} f^n_{ij}g^n_{ij}h^2, \quad \|f^n\|^2 = (f^n, f^n).$$

By introduce the induction hypothesis

$$\sup_{0\leq n\leq L}\{\|\xi^n\|, \|\zeta^n\|, \|\delta_x\zeta^n\| + \|\delta_y\zeta^n\|\} \to 0, (h, \Delta t) \to 0. \tag{13}$$

and some techniques and applying discrete Gronwall Lemma, the following theorem can be obtained.

Theorem 3.1. *Suppose that the solution of the problem (5) (6) satisfies the condition (10) and the time and space discretization satisfy the relationship $\Delta t = O(h^2)$, then the following error estimate holds for the modified upwind difference scheme (11) (12):*

$$\begin{aligned} &\|c_1 - C_1\|_{\overline{L^\infty}([0,T];h^1)} + \|c_2 - C_2\|_{\overline{L^\infty}([0,T];l^2)} + \|d_t\,(c_1 - C_1)\|_{\overline{L^2}([0,T];l^2)} \\ &+ \|d_t\,(c_2 - C_2)\|_{\overline{L^2}([0,T];l^2)} \leq M^*\left\{\Delta t + h^2\right\}, \end{aligned} \tag{14}$$

where

$$\|g\|_{\overline{L^\infty}(J;X)} = \sup_{n\Delta t\leq T}\|g^n\|_X, \quad \|g\|_{\overline{L^2}(J;X)} = \sup_{n\Delta t\leq T}\left\{\sum_{n=0}^{L}\|g^n\|^2_X\,\Delta t\right\}^{\frac{1}{2}},$$

$$M^* = M^*\left\{\left\|\frac{\partial^2 c_1}{\partial t^2}\right\|_{L^\infty}, \left\|\frac{\partial^2 c_2}{\partial t^2}\right\|_{L^\infty}, \|c_1\|_{L^\infty(W^{4,\infty})}, \|c_1\|_{W^{1,\infty}}\right\}.$$

Proof. (6) and (12) can be combined to get:

$$b_{ij}\frac{\xi^{n+1}_{ij} - \xi^n_{ij}}{\Delta t} = \omega\left(\zeta^{n+1}_{ij} - \xi^{n+1}_{ij}\right) - \mu_{2,ij}\xi^{n+1}_{ij} + \varepsilon_2(x_{ij}, t^{n+1}) \tag{15}$$

where $\varepsilon^{n+1}_{2,ij} \leq M\left\{\left\|\frac{\partial^2 c_2}{\partial t^2}\right\|_{L^\infty}\right\}\Delta t$, then $\varepsilon_2 = O\left(\Delta t\right)$.

Suppose the time step and the space step satisfy the relationship $\Delta t = O\left(h^2\right)$. and introduce the hypothesis (13)

$$\sup_{0\leq n\leq L}\{\|\xi^n\|, \|\zeta^n\|, \|\delta_x\zeta^n\| + \|\delta_y\zeta^n\|\} \to 0, \quad (h, \Delta t) \to 0.$$

Take the inner product of the relation (15) against the test function $\delta_t\xi^n_{ij} = \xi^{n+1}_{ij} - \xi^n_{ij} = d_t\xi^n_{ij}\Delta t$, then

$$(bd_t\xi^n, d_t\xi^n)\,\Delta t = \left(\omega\left(\zeta^{n+1} - \xi^{n+1}\right), d_t\xi^n\right)\Delta t - \left(\mu_2\xi^{n+1}, d_t\xi^n\right)\Delta t + \left(\varepsilon^{n+1}_{2,ij}, d_t\xi^n\right)\Delta t.$$

Thus, we get:

$$\|d_t\xi^n\|^2\Delta t \le M\left(\left\|\zeta^{n+1}\right\|^2+\left\|\xi^{n+1}\right\|^2\right)\Delta t + M\left((\Delta t)^2\right)\Delta t. \tag{16}$$

From (5) and (11), we get:

$$\begin{aligned}
& a_{ij}\frac{\zeta_{ij}^{n+1}-\zeta_{ij}^{n}}{\Delta t}+b_{ij}\frac{\xi_{ij}^{n+1}-\xi_{ij}^{n}}{\Delta t}+\delta_{U^{n+1},x}\zeta_{ij}^{n+1}+\delta_{W^{n+1},y}\zeta_{ij}^{n+1}\\
+ \ & \mu_{1,ij}\zeta_{ij}^{n+1}+\mu_{2,ij}\xi_{ij}^{n+1}\\
= \ & \{(1+\tfrac{h}{2}|U_{ij}^{n+1}|D_{ij}^{-1})\delta_{\bar{x}}(D\delta_x\zeta_{ij}^{n+1})+(1+\tfrac{h}{2}|W_{ij}^{n+1}|D_{ij}^{-1})\delta_{\bar{y}}(D\delta_y\zeta_{ij}^{n+1})\}\\
+ \ & \varepsilon_1(x_{ij},t^{n+1}),\quad 1\le i,j\le N-1
\end{aligned} \tag{17}$$

$$\zeta_{ij}^{n+1}=0,\quad x_{ij}\in\partial\Omega_1. \tag{18}$$

where, we have used the fact that

$$\begin{aligned}
&\delta_{U^{n+1},x}c_{ij}^{n+1}-\left(U^{n+1}\frac{\partial c^{n+1}}{\partial x}\right)_{ij}\\
=&\frac{U_{ij}^{n+1}+|U_{ij}^{n+1}|}{2}D_{ij}^{-1}D_{i-\frac12,j}\delta_{\bar{x}}c_{ij}^{n+1}+\frac{U_{ij}^{n+1}-|U_{ij}^{n+1}|}{2}D_{ij}^{-1}D_{i+\frac12,j}\delta_{x}c_{ij}^{n+1}-\left(U^{n+1}\frac{\partial c^{n+1}}{\partial x}\right)_{ij}\\
=&-\frac{h}{2}\left|U_{ij}^{n+1}\right|D_{ij}^{-1}\delta_{\bar{x}}\left(D\delta_x c^{n+1}\right)_{ij}+O\left(\left\|\frac{\partial^3 c}{\partial x^3}\right\|_{L^\infty(L^\infty)}\right)h^2,
\end{aligned}$$

$$\begin{aligned}
&\delta_{W^{n+1},y}c_{ij}^{n+1}-\left(W^{n+1}\frac{\partial c^{n+1}}{\partial y}\right)_{ij}\\
=&\frac{W_{ij}^{n+1}+|W_{ij}^{n+1}|}{2}D_{ij}^{-1}D_{i,j-\frac12}\delta_{\overline{y}}c_{ij}^{n+1}+\frac{W_{ij}^{n+1}-|W_{ij}^{n+1}|}{2}D_{ij}^{-1}D_{i,j+\frac12}\delta_{y}c_{ij}^{n+1}-\left(W^{n+1}\frac{\partial c^{n+1}}{\partial y}\right)_{ij}\\
=&-\frac{h}{2}\left|W_{ij}^{n+1}\right|D_{ij}^{-1}\delta_{\overline{y}}\left(D\delta_y c^{n+1}\right)_{ij}+O\left(\left\|\frac{\partial^3 c}{\partial y^3}\right\|_{L^\infty(L^\infty)}\right)h^2,
\end{aligned}$$

and the facts that

$$\begin{aligned}
&\frac{\partial}{\partial x}\left(D\frac{\partial c^{n+1}}{\partial x}\right)_{ij}-\left(1+\frac{h}{2}\left|U_{ij}^{n+1}\right|D_{ij}^{-1}\right)^{-1}\delta_{\bar{x}}\left(D\delta_x c^{n+1}\right)_{ij}\\
= \ &\frac{h}{2}\left|U_{ij}^{n+1}\right|D_{ij}^{-1}\delta_{\bar{x}}\left(D\delta_x c^{n+1}\right)_{ij}+O\left(\left\|\frac{\partial^4 c}{\partial x^4}\right\|_{L^\infty(L^\infty)}\right)h^2.
\end{aligned}$$

$$\begin{aligned}
&\frac{\partial}{\partial y}\left(D\frac{\partial c^{n+1}}{\partial y}\right)_{ij}-\left(1+\frac{h}{2}|W_{ij}^{n+1}|D_{ij}^{-1}\right)^{-1}\delta_{\bar{y}}\left(D\delta_y c^{n+1}\right)_{ij}\\
= \ &\frac{h}{2}\left|W_{ij}^{n+1}\right|D_{ij}^{-1}\delta_{\bar{y}}\left(D\delta_y c^{n+1}\right)_{ij}+O\left(\left\|\frac{\partial^4 c}{\partial y^4}\right\|_{L^\infty(L^\infty)}\right)h^2.
\end{aligned}$$

Then, we get the following estimates:

$$\begin{aligned}
&a_{ij}\frac{c_{1,ij}^{n+1}-c_{1,ij}^{n}}{\Delta t}+b_{ij}\frac{c_{2,ij}^{n+1}-c_{2,ij}^{n}}{\Delta t}+\delta_{U^{n+1},x}c_{1,ij}^{n+1}+\delta_{W^{n+1},y}c_{1,ij}^{n+1}\\
&-\left\{\left(1+\tfrac{h}{2}\tfrac{|U_{ij}^{n+1}|}{D_{ij}}\right)^{-1}\delta_{\bar{x}}(D\delta_x c_{ij}^{n+1})+\left(1+\tfrac{h}{2}\tfrac{|W_{ij}^{n+1}|}{D_{ij}}\right)^{-1}\delta_{\bar{y}}(D\delta_y c_{ij}^{n+1})\right\}\\
&+\mu_{1,ij}c_{1,ij}^{n+1}+\mu_{2,ij}c_{2,ij}^{n+1}-\gamma_{1,ij}-\gamma_{2,ij}=\varepsilon_{1,ij}^{n+1}.
\end{aligned} \tag{19}$$

where

$$\varepsilon_{1,ij}^{n+1} \leq M \left\{ \left\| \frac{\partial^2 c_1}{\partial t^2} \right\|_{L^\infty(L^\infty)}, \left\| \frac{\partial^2 c_2}{\partial t^2} \right\|_{L^\infty(L^\infty)}, \|c_1\|_{L^\infty(W^{4,\infty})} \right\} (\Delta t + h^2.)$$

Take the inner product of the relation (17) against the test function $\delta_t \zeta_{ij}^n = \zeta_{ij}^{n+1} - \zeta_{ij}^n = d_t \zeta_{ij}^n \Delta t$, we get

$$\begin{aligned} & (a d_t \zeta^n, d_t \zeta^n)\, \Delta t + (b d_t \xi^n, d_t \zeta^n)\, \Delta t \\ + & \left(\delta_{U^{n+1},x} \zeta^{n+1}, d_t \zeta^n\right) \Delta t + \left(\delta_{W^{n+1},y} \zeta^{n+1}, d_t \zeta^n\right) \Delta t \\ + & \left(D \delta_x \zeta^{n+1}, \delta_x [\left(1 + \tfrac{h}{2} \left|U^{n+1}\right| D^{-1}\right)^{-1} \left(\zeta^{n+1} - \zeta^n\right)]\right) \\ + & \left(D \delta_y \zeta^{n+1}, \delta_y [\left(1 + \tfrac{h}{2} \left|W^{n+1}\right| D^{-1}\right)^{-1} \left(\zeta^{n+1} - \zeta^n\right)]\right) \\ = & \left(-\mu_1 \zeta^{n+1}, d_t \zeta^n\right) \Delta t + \left(-\mu_2 \xi^{n+1}, d_t \zeta^n\right) \Delta t + \left(\varepsilon_{1,ij}^{n+1}, d_t \zeta^n\right) \Delta t. \end{aligned} \tag{20}$$

The term on the left-hand side of (20) can be estimated by

$$\begin{aligned} & \left(D \delta_x \zeta^{n+1}, \delta_x [(1 + \tfrac{h}{2} \left|U^{n+1}\right| D^{-1})^{-1} (\zeta^{n+1} - \zeta^n)]\right) \\ = & \left(D \delta_x \zeta^{n+1}, \delta_x (1 + \tfrac{h}{2} |U^{n+1}| D^{-1})^{-1} (\zeta^{n+1} - \zeta^n)\right) \\ + & \left(D \delta_x \zeta^{n+1}, (1 + \tfrac{h}{2} |U^{n+1}| D^{-1})^{-1} \delta_x (\zeta^{n+1} - \zeta^n)\right). \end{aligned}$$

Note that

$$\begin{aligned} \delta_x \left(1 + \frac{h}{2} |U^{n+1}| D^{-1}\right)^{-1} &= \frac{\frac{h}{2} \left(\left|U_{i,j}^{n+1}\right| - \left|U_{i+1,j}^{n+1}\right|\right) D_{ij}^{-1}}{\left(1 + \frac{h}{2} \left|U_{i+1,j}^{n+1}\right| D_{ij}^{-1}\right) \left(1 + \frac{h}{2} \left|U_{i,j}^{n+1}\right| D_{ij}^{-1}\right)} \\ &\leq \frac{\frac{h}{2} \left|\delta_x U_{ij}^{n+1}\right| D_{ij}^{-1}}{\left(1 + \frac{h}{2} \left|U_{i+1,j}^{n+1}\right| D_{ij}^{-1}\right) \left(1 + \frac{h}{2} \left|U_{i,j}^{n+1}\right| D_{ij}^{-1}\right)}. \end{aligned}$$

then

$$\begin{aligned} & \left(D \delta_x \zeta^{n+1}, \delta_x [(1 + \tfrac{h}{2} \left|U^{n+1}\right| D^{-1})^{-1} (\zeta^{n+1} - \zeta^n)]\right) \\ \geq & \frac{1}{2} \left(D \delta_x \zeta^{n+1}, \left(1 + \tfrac{h}{2} \left|U^{n+1}\right| D^{-1}\right)^{-1} \delta_x \zeta^{n+1}\right) \\ & - \left(D \delta_x \zeta^n, \left(1 + \tfrac{h}{2} \left|U^{n+1}\right| D^{-1}\right)^{-1} \delta_x \zeta^n\right) - \left\|\delta_x \zeta^{n+1}\right\|^2 \Delta t - \epsilon \left\|d_t \zeta^n\right\|^2 \Delta t. \end{aligned}$$

Similarly, we have

$$\begin{aligned} & \left(D \delta_y \zeta^{n+1}, \delta_y \left[\left(1 + \tfrac{h}{2} \left|W^{n+1}\right| D^{-1}\right)^{-1} \left(\zeta^{n+1} - \zeta^n\right)\right]\right) \\ \geq & \frac{1}{2} \left(D \delta_y \zeta^{n+1}, \left(1 + \tfrac{h}{2} \left|W^{n+1}\right| D^{-1}\right)^{-1} \delta_y \zeta^{n+1}\right) \\ & - \left(D \delta_y \zeta^n, \left(1 + \tfrac{h}{2} \left|W^{n+1}\right| D^{-1}\right)^{-1} \delta_y \zeta^n\right) - \left\|\delta_y \zeta^{n+1}\right\|^2 \Delta t - \epsilon \left\|d_t \zeta^n\right\|^2 \Delta t. \end{aligned}$$

Using the fact that

$$\left(\delta_{U^{n+1},x} \zeta^{n+1}, d_t \zeta^n\right) \Delta t \leq M \left\|\delta_x \zeta^{n+1}\right\|^2 \Delta t + \epsilon \left\|d_t \zeta^n\right\|^2 \Delta t,$$

$$\left(\delta_{W^{n+1},y} \zeta^{n+1}, d_t \zeta^n\right) \Delta t \leq M \left\|\delta_y \zeta^{n+1}\right\|^2 \Delta t + \epsilon \left\|d_t \zeta^n\right\|^2 \Delta t.$$

Then, we have

$$
\begin{aligned}
& \|d_t\zeta^n\|^2\Delta t + \|\delta_x\zeta^{n+1}\|^2 - \|\delta_x\zeta^n\|^2 + \|\delta_y\zeta^{n+1}\|^2 - \|\delta_y\zeta^n\|^2 \\
\leq \; & M\{\|d_t\xi^n\|^2 + \|\nabla_h\zeta^{n+1}\|^2 + \|\nabla_h\zeta^n\|^2 + \|\zeta^{n+1}\|^2 + \|\xi^{n+1}\|^2\}\Delta t \\
& +M\{(\Delta t)^2 + h^4\}\Delta t.
\end{aligned} \tag{21}
$$

If (21), is summed in time for $0 \leq n \leq L$, we have

$$
\begin{aligned}
& \sum_{n=0}^{L} \|d_t\zeta^n\|^2 \Delta t + \left\|\nabla_h\zeta^{L+1}\right\|^2 \\
\leq \; & M\sum_{n=0}^{L}\left\{\|d_t\xi^n\|^2 + \|\nabla_h\zeta^{n+1}\|^2 + \|\zeta^{n+1}\|^2 + \|\xi^{n+1}\|^2\right\}\Delta t \\
+ \; & M\sum_{n=0}^{L}\left\{(\Delta t)^2 + h^4\right\}\Delta t.
\end{aligned} \tag{22}
$$

Similarly, for (16), we sum in time for $0 \leq n \leq L$ and get

$$
\sum_{n=0}^{L} \|d_t\xi^n\|^2 \Delta t \leq M\sum_{n=0}^{L}\left\{\left\|\zeta^{n+1}\right\|^2 + \left\|\xi^{n+1}\right\|^2 + (\Delta t)^2\right\}\Delta t. \tag{23}
$$

Noting that $\zeta^0 = \xi^0 = 0$, we have

$$
\begin{aligned}
\left\|\zeta^{L+1}\right\|^2 &\leq M\sum_{n=0}^{L}\|\zeta^n\|^2\Delta t + \epsilon\sum_{n=0}^{L}\|d_t\zeta^n\|^2\Delta t, \\
\left\|\xi^{L+1}\right\|^2 &\leq M\sum_{n=0}^{L}\|\xi^n\|^2\Delta t + \epsilon\sum_{n=0}^{L}\|d_t\xi^n\|^2\Delta t.
\end{aligned} \tag{24}
$$

then

$$
\begin{aligned}
& \sum_{n=0}^{L}\left(\|d_t\zeta^n\|^2\Delta t + \|d_t\xi^n\|^2\Delta t\right) + \left\|\zeta^{L+1}\right\|_1^2 + \left\|\xi^{L+1}\right\|^2 \\
\leq \; & M\sum_{n=0}^{L}\left\{\|\nabla_h\zeta^n\|^2 + \|\zeta^n\|^2 + \|\xi^n\|^2\right\}\Delta t + M\left\{(\Delta t)^2 + h^4\right\}.
\end{aligned}
$$

An application of the Gronwall lemma shows that

$$
\sum_{n=0}^{L}\left(\|d_t\zeta^n\|^2 + \|d_t\xi^n\|^2\right)\Delta t + \left\|\zeta^{L+1}\right\|_1^2 + \left\|\xi^{L+1}\right\|^2 \leq M\left\{(\Delta t)^2 + h^4\right\}. \tag{25}
$$

It is easy to know that the induction hypothesis holds. Thus, we get the proof of the theorem 3.1.

□

4. Numerical Examples

For the nonequilubrium transport model in one dimension [7, 8, 16],

$$
\begin{aligned}
\beta R\frac{\partial c_1}{\partial t} &= D\frac{\partial^2 c_1}{\partial x^2} - \frac{\partial c_1}{\partial x} - \omega(c_1 - c_2) - \mu_1 c_1 + \gamma_1(x), \\
(1-\beta)R\frac{\partial c_2}{\partial t} &= \omega(c_1 - c_2) - \mu_2 c_2 + \gamma_2(x).
\end{aligned} \tag{26}
$$

Van Genuchten[7, 8, 16] presented the analytical solutions for different initial and boundary conditions. In Fig.1 and Fig. 2, the analytical solution and the solution of modified upwind finite difference method are compared. It is shown that the modified upwind finite difference method(MUDM) is more accurate that upwind difference method(UDM).

Example 1. Initial Value Problem with Stepwise Initial Distribution.We choose $D = 0.1, \beta = 0.5, R = 2, \omega = 1, \nu_1 = \nu_2 = 0.2, \gamma_1 = \gamma_2 = 0, \Delta t = 0.0025$ and $h = 0.05$. Let

$$c_{1,0}(x) = c_{2,0}(x) = \begin{cases} 0.3, & 0 \le x < 0.5, \\ 1, & 0.5 \le x < 1. \\ 0.1, & 1 \le x \end{cases}$$

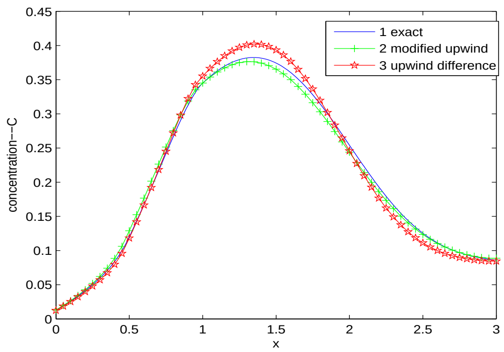

FIGURE 1. Calculated resident equilibrium C1 distribution versus distance x at T = 1

Example 2. Boundary Value Problem with Stepwise Boundary Condition. We choose $D = 0.25, \beta = 0.5, R = 2, \nu_1 = \nu_2 = 0, \gamma_1 = \gamma_2 = 0.$ and $\Delta t = 0.006, h = 0.08$. Assume that the initial concentration is zero. The boundary condition is given by

$$c_0(t) = \begin{cases} 1, & 0 < t \le 3, \\ 0, & t > 3. \end{cases}$$

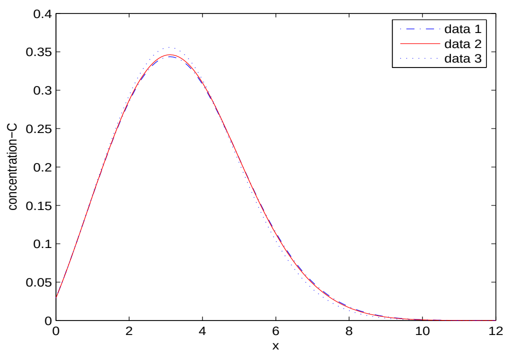

FIGURE 2. Calculated resident equilibrium C1 distribution versus distance x at T = 3

In Fig.2, data 2 is the analytical solution c1 at T = 3. data 1 is obtained by modified upwind finite difference method and data 3 is obtained by upwind finite difference method.

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