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Analytical model for coupled multispecies advective-dispersive transport subject to rate-limited sorption

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Abstract

Mathematical models that analytically solve a set of simultaneous multispecies advection-dispersion transport equations coupled with a series of chemical reactions are cost-effective tools for predicting the plume migration of dissolved chlorinated solvents and nitrogen chains. However, few analytical solutions for coupled reactive multispecies transport equations have appeared in the literature. For convenience of mathematical derivation, most analytical models currently used to simulate multispecies transport assume instantaneous equilibrium between the dissolved and sorbed phases of the contaminant. However, research has demonstrated that rate-limited sorption process can have a profound effect upon solute transport in the subsurface environment. Making the instantaneous equilibrium sorption assumption precludes consideration of potential effects of the rate-limited sorption. This study presents a novel analytical model for simulating the migrations of plumes of decaying or degradable contaminants subject to rate-limited sorption. The derived analytical model is then applied to investigate the effects of the rate-limited sorption on the plume migration of degradable contaminants. Results show that the kinetic sorption rate constant has significant impacts on the plume migration of degradable contaminants. Increasing the kinetic sorption rate constant results in a reduction of predicted concentration for all species in the degradable contaminants while the equilibrium-controlled sorption model lead to significant underestimation of the concentrations of degradable contaminants under conditions with low sorption Damköler number, $Da_i = \frac{\beta_i L}{v}$. The equilibrium-controlled sorption model agrees well with the rate-limited sorption model when the Damköler number is greater than 2 to 3 order of magnitude. The invalidity of the equilibrium-controlled sorption model of low

Damköler number case implies that the health risk could be underestimated if such a model is used for assessing the concentrations of the degradable contaminants in the health risk model.

Keywords: analytical model; multispecies transport; equilibrium-controlled sorption; rate-limited sorption, sorption reaction rate constant, Damköler number

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1. Introduction

Given growing concern and recognition of the potential threat of environmental contaminants to human health, researchers are placing emphasis on understanding the fate and transport of contaminants dissolved in the groundwater system. Study of contaminant transport problems requires the use of appropriate modeling tools. Mathematical models that apply analytical or numerical approaches to solve the advection-dispersion equations (ADEs) have been demonstrated to be effective for comprehending the transport behavior of contaminants in subsurface environments. Analytical modelling is an essential and efficient tool with a variety of applications, such as testing and validating numerical formulations, providing approximate analysis of pollution threat scenarios, performing sensitivity analysis to investigate how various parameters affect the processes of contaminant transport, extrapolating results over large times or extensive spatial scales and last but not least, as a screening tool. A number of analytical models has been derived for describing single-species transport of various contaminants (Batu, 1989, 1993, 1996; Chen et al., 2008a, b; 2011a, b; 2016b, 2017; Chen and Liu, 2011; Gao et al., 2010, 2012, 2013; Leij et al., 1991, 1993; Liang et al., 2016; Park and Zhan, 2001; Pérez Guerrero and Skaggs, 2010; Pérez Guerrero et al., 2013; van Genuchten and Alves, 1982; Yeh, 1981; Zhan et al., 2009). However, the transport processes for some contaminants of concern such as radionuclides, nitrogenous and dissolved chlorinated solvents generally involve a more complicated series of first-order or pseudo first-order decay or degradation chain reactions which also play a decisive role affecting the migration of those decaying or degradable contaminants.

Single-species transport analytical models are unable to account for mass

92 transformation from the parent species to the daughter species of degradable
93 contaminants. Efforts to develop multispecies transport analytical models are required
94 in order to more accurately evaluate the process of monitored natural attenuation (MNA)
95 of chlorinated solvent contaminated site. However, at the present time, only a small
96 number of multispecies transport analytical models can be found in the literature as
97 compared to the large number of single-species transport analytical models although
98 significant contributions have been made to develop multispecies transport analytical
99 models over the past decades (Chen et al., 2012a, b, 2016a; Cho, 1971; Clement, 2001;
100 Lunn et al., 1996; Mieles and Zhan, 2012; Pérez Guerrero et al., 2009, 2010; Quezada
101 et al., 2004; Srinivasan and Clement, 2008a, b; Sudicky et al., 2013; Sun and Clement,
102 1999; Sun et al., 1999a, b; van Genuchten, 1985). Currently, all these multispecies
103 transport analytical models have been derived by considering equilibrium-controlled
104 sorption process. By making the equilibrium-controlled assumption, the rate of mass
105 adsorption and desorption between the dissolved and sorbed phases is considered to
106 occur rapidly in comparison to the time-scale required for the movement of
107 contaminants through a porous medium. When the sorption process is not sufficiently
108 fast compared to the time-scale required for transport in the dissolved phase, the
109 sorption behavior should be described as a rate-limited process.

110 It has been shown that rate-limited sorption process can have a profound effect on
111 the transport behaviors of the sorbing contaminants (van Genuchten and Wierenga,
112 1976; Nkedi-Kizza et al., 1982; Goltz and Roberts, 1988; Ball, 1989; Brusseau and Rao,
113 1989). Brusseau et al. (1991) sought to understand the influence of rate-limited sorption
114 and nonequilibrium transport on the movement of hydrophobic organic chemicals in
115 various low-organic carbon aquifer materials. Their results showed that contaminants

116 moving in a slowly flowing natural groundwater system could be successfully
117 simulated with the equilibrium-controlled sorption model. However, appropriate
118 models based on nonequilibrium or rate-limited sorption processes are needed for cases
119 when the pore water velocity is so fast that local instantaneous equilibrium cannot be
120 attained to correctly predict the solute transport behavior. Goltz and Oxley (1991)
121 demonstrated that rate-limited sorption has a significant impact upon the efficiency of
122 aquifer decontamination by pumping. The use of a rate-limited sorption model can be
123 very different from the results obtained from the equilibrium-controlled sorption model
124 in predicting contaminant concentrations and remediation time (Haggerty and Gorelick,
125 1994). Clement et al. (2004) also pointed out that the commonly used equilibrium-
126 controlled sorption approach might not be valid in some environmental assessment
127 cases. They considered a rate-limited sorption approach to simulate more realistic
128 multispecies reactive transport using the three-dimensional code RT3D (Clement,
129 1997).

130 The above review suggests that it is urgent to develop an advanced multispecies
131 reactive transport analytical model to cope with more complicated sorption process in
132 the subsurface system. To the best of our knowledge, a multispecies transport analytical
133 model subject to rate-limited sorption has not yet been developed. Thus, the objective
134 of this study is to develop a novel analytical model for describing multispecies reactive
135 transport subject to rate-limited sorption. A set of first-order reversible kinetic reaction
136 equations that represents the rate-limited sorption process between the dissolved and
137 sorbed phases of each individual species are coupled to a set of simultaneous advection-
138 dispersion transport equations. The key feature of this work is that the sorption
139 mechanisms of each individual species is considered as first-order reversible kinetic

rather than equilibrium-controlled. The correctness of the derived analytical models is verified by comparisons of the computational results with those obtained from the multispecies transport analytical model subject to equilibrium-controlled sorption and numerical models for solving the same governing equations using the Laplace transform finite difference (LTFD) method (Moridis and Reddell, 1991). The derived analytical model is then applied to investigate the effects of the rate-limited sorption on the multispecies transport of degradable contaminants. Note that the analytical solutions with concise expressions are obtained by assuming that degradation reactions only occur in the dissolved phase. Thus, the application of the derived analytical model should consider and evaluate if the degradation reactions of the concerned degradable contaminants occur only in the dissolved phase.

2. Development of a multispecies analytical model

This study considers the multispecies transport of decaying or degradable contaminants subject to rate-limited sorption. The contaminant source considered is chlorinated solvents dissolved into the aqueous phase from a residual non-aqueous phase liquid (NAPL). After the contaminants enter the dissolved phase, transport is controlled by the movement of the groundwater flow, hydrodynamic dispersion, as well as the degradation reaction and the rate-limited sorption. On the microscopic scale, sorption refers to the exchange of contaminants between the dissolved and sorbed phases. Instead of the widely used equilibrium-controlled sorption assumption, this study considers rate-limited (nonequilibrium-controlled) sorption. The rate-limited sorption process is often represented as a first-order reversible kinetic reaction. When dissolved contaminants migrate in the groundwater flow system, there is a loss of

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contaminant mass in the dissolved phase due to the degradation reactions and rate-limited sorption. One key feature of the so-called multispecies model is that the mass accumulation of the predecessors is also considered. Based on the conceptual description, the governing equations for describing one-dimensional transport of degradable contaminants involving an arbitrary number of species undergoing a series of first-order degradation reactions in the dissolved phase and first-order reversible kinetic sorption reaction between the dissolved and sorbed phases are

$$D\frac{\partial^2 C_1(x,t)}{\partial x^2} - v\frac{\partial C_1(x,t)}{\partial x} - \lambda_1 C_1(x,t) - \frac{\beta_1}{\theta}\left(C_1(x,t) - \frac{S_1(x,t)}{K_1}\right) = \frac{\partial C_1(x,t)}{\partial t} \tag{1a}$$

$$D\frac{\partial^2 C_i(x,t)}{\partial x^2} - v\frac{\partial C_i(x,t)}{\partial x} - \lambda_i C_i(x,t) + \lambda_{i-1} C_{i-1}(x,t) - \frac{\beta_i}{\theta}\left(C_i(x,t) - \frac{S_i(x,t)}{K_i}\right) = \frac{\partial C_i(x,t)}{\partial t} \qquad i = 2,\ldots,N \tag{1b}$$

$$\rho_b \frac{\partial S_i(x,t)}{\partial t} = \beta_i\left(C_i(x,t) - \frac{S_i(x,t)}{K_i}\right) \qquad i = 1,\ldots,N \tag{2}$$

where $C_i(x,t)$ is the concentration of species i in the dissolved phase [ML^{-3}]; $S_i(x,t)$ is the concentration of species i in the sorbed phase [MM^{-1}]; v is the average uniform pore-water velocity [LT^{-1}]; D is the hydrodynamic dispersion coefficient [L^2T^{-1}]; x is the spatial coordinate [L]; t is the time [T]; θ is the porosity; ρ_b is the bulk dry density of the solid grain [ML^{-3}]; K_i is the distribution coefficient of species i [$M^{-1}L^3$]; λ_i is the first-order degradation rate constant of species i in the dissolved phase [T^{-1}]; β_i is the first-order sorption rate constant of species i between the dissolved and

sorbed phases [T^{-1}] (referred to as the kinetic sorption rate constant thereafter); N is the total species number of degradable contaminants. Eqs. (1a) and (1b) describe the advective-dispersive transport of the dissolved phase of degradable contaminants subject to a series of first-order degradation reactions and first-order reversible kinetic (rate-limited) mass transfer due to sorption. The mass transfer between the dissolved and sorbed phases of multiple species is represented by a first-order reversible kinetic reaction coupled to the equations so that the assumption of rate-limited sorption can be considered. Eq. (2) accounts for mass conservation in the sorbed phase of multiple species. Note that these equations consider that the degradation reactions occur only in both the dissolved phase. The fourth term on the left-hand side of Eq. (1a) and the fifth term on the left-hand side of Eq. (1b) quantify the mass accumulation from the predecessor species between the dissolved and sorbed phases. The above coupled equations described in Eqs. (1a), (1b) and (2) must be solved simultaneously to obtain the solutions for each individual species in the dissolved and sorbed phases. It should be pointed out that, for the sake of clarity, the porous medium is considered homogeneous and all the aforementioned transport parameters of the porous medium are assumed to be independent of time and space.

The medium is initially assumed to be free of the individual species mass of a decay chain in both the dissolved and sorbed phases:

$$C_i(x,t=0)=0 \qquad i=1,\ldots,N \qquad (3)$$

$$S_i(x,t=0)=0 \qquad i=1,\ldots,N \qquad (4)$$

There is assumed to be a continuous constant concentration of dissolved phase contaminant sources. The contaminant sources are treated mathematically as third-type boundary conditions and formulated as

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$$-D\frac{\partial C_i(x=0,t)}{\partial x}+vC_i(x=0,t)=vc_{i,0} \qquad i=1,\ldots,N \qquad (5)$$

where $c_{i,0}$ is the source of the constant concentration of species *i* at the inlet boundary [ML^{-3}]. The third-type boundary conditions in Eq. (5) is regarded as satisfying the principle of mass conservation of each individual species at the inlet boundary. A finite-domain subsurface porous medium system is considered in this study. Considering the mass conservation of each individual species at the outlet boundary, a second-type boundary condition with zero concentration gradient is used and can be mathematically expressed as

$$\frac{\partial C_i(x=L,t)}{\partial x}=0 \qquad i=1,\ldots,N \qquad (6)$$

where L is the length of the transport system [L].

The derivation of the analytical solutions to the initial-boundary value problems as defined in Eqs. (1a), (1b) and (2)-(6) is facilitated by reducing the number of model parameters. The coupled governing equations, initial conditions and boundary conditions are transformed into dimensionless forms as follows:

$$\frac{1}{Pe}\frac{\partial {C_1}^2(X,T)}{\partial X^2}-\frac{\partial C_1(X,T)}{\partial X}-\Lambda_1 C_1(X,T) -\frac{\mathrm{B}_1}{\theta}\left(C_1(X,t)-\frac{S_1(X,T)}{K_1}\right)=\frac{\partial C_1(X,T)}{\partial T} \qquad i=2,\ldots,N \qquad (6a)$$

$$\frac{1}{Pe}\frac{\partial^2 C_i(X,T)}{\partial X^2}-\frac{\partial C_i(X,T)}{\partial X}-\Lambda_i C_i(X,T) +\Lambda_{i-1}C_{i-1}(X,T)-\frac{\mathrm{B}_i}{\theta}\left(C_i(X,T)-\frac{S_i(X,T)}{K_i}\right) =\frac{\partial C_i(X,T)}{\partial T} \qquad (6b)$$

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$$K_i\rho_b\frac{\partial S_i(X,T)}{\partial T}=\mathrm{B}_i\left(K_iC_i(X,T)-S_i(X,T)\right) \qquad i=1,\ldots,N \qquad (7)$$

$$C_i(X,T=0)=0 \qquad i=1,\ldots,N \qquad (8)$$

$$S_i(X,T=0)=0 \qquad i=1,\ldots,N \qquad (9)$$

$$-\frac{1}{Pe}\frac{\partial C_i(X=0,T)}{\partial X}+C_i(X=0,T)=c_{i,0} \qquad i=1,\ldots,N \qquad (10)$$

$$\frac{\partial C_i(X=1,T)}{\partial X}=0 \qquad i=1,\ldots,N \qquad (11)$$

where $X=\frac{x}{L}$, $T=\frac{vt}{L}$, $Pe=\frac{vL}{D}$, $\Lambda_i=\frac{\lambda_iL}{v}$, $\mathrm{B}_i=\frac{\beta_iL}{v}$, $\Gamma_i=\frac{\gamma_iL}{v}$.

The solution strategy adopted in this study is an extension of an efficient method for analytically solving a set of coupled advection-dispersion equations proposed by Chen et al. (2012a).

The first step is to take the Laplace transform with respect to T. After the Laplace transform, Eqs. (6a), (6b) and (7) can be expressed as

$$\frac{1}{Pe}\frac{d^2C_1^{\,L}(X,s)}{dX^2}-\frac{dC_1^{\,L}(X,s)}{dX}-\Lambda_1C_1^{\,L}(X,s)-\frac{\mathrm{B}_1}{\theta}\left(C_1^{\,L}(X,s)-\frac{S_1^{\,L}(X,s)}{K_1}-sC_1^{\,L}(X,s)\right)=0 \qquad (12a)$$

$$\frac{1}{Pe}\frac{d^2C_i^{\,L}(X,s)}{dX^2}-\frac{dC_i^{\,L}(X,s)}{dX}-\Lambda_iC_i^{\,L}(X,s)+\Lambda_{i-1}C_{i-1}^{\,L}(X,s)-\frac{\mathrm{B}_i}{\theta}\left(C_i^{\,L}(X,s)-\frac{S_i^{\,L}(X,s)}{K_i}-sC_i^{\,L}(X,s)\right)=0 \qquad i=2,\ldots,N \qquad (12b)$$

$$sK_i\rho_bS_i^{\,L}(X,s)=\mathrm{B}_i\left(K_iC_i^{\,L}(X,s)-S_i^{\,L}(X,s)\right) \qquad (13)$$

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where $C_i^L(X,s)=\int_0^\infty e^{-sT}C_i(X,T)dT$ and $S_i^L(X,s)=\int_0^\infty e^{-sT}S_i(X,T)dT$, s is the Laplace transform parameter.

Then, we can solve Eq. (13) algebraically for the transform of the sorbed phase concentration for each individual species ($S_i^L(X,s)$) and $S_i^L(X,s)$ is conveniently expressed in terms of the transform of dissolved phase concentration for each individual species ($C_i^L(X,s)$) Through substitution of the relations between $S_i^L(X,s)$ $C_i^L(X,s)$, Eqs. (12a) and (12b) can be expressed as

$$\frac{1}{Pe}\frac{d^2C_1^L(X,s)}{dX^2}-\frac{dC_1^L(X,s)}{dX}-\Theta_1(s)C_1^L(X,s)=0 \qquad (14a)$$

$$\frac{1}{Pe}\frac{d^2C_i^L(X,s)}{dX^2}-\frac{dC_i^L(X,s)}{dX}-\Theta_i(s)C_i^L(X,s) = -\Lambda_{i-1}C_{i-1}^L(X,s) \qquad i=2,\ldots,N \qquad (14b)$$

where $\Theta_i(s)=s+\Lambda_i+\frac{\mathrm{B}_i}{\theta}\frac{sK_i\rho_b}{sK_i\rho_b+\mathrm{B}_i}$.

The boundary conditions after the Laplace transform become

$$-\frac{1}{Pe}\frac{dC_i^L(X=0,s)}{dX}+C_i^L(X=0,s)=\frac{c_{i,0}}{s} \qquad i=1,\ldots,N \qquad (15)$$

$$\frac{dC_i^L(X=1,s)}{dX}=0 \qquad i=1,\ldots,N \qquad (16)$$

Next, the integral transform technique is used to eliminate the X variable and reduce the system of the ordinary differential equations into a set of linear algebraic equations. Prior to applying the integral transform technique, we need to homogenize

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the boundary condition in Eq. (15) and convert Eqs. (14a) and (14b) into purely diffusive equations. The homogenization of the boundary conditions in Eq. (15) is done with a change of variable

$$C_i^L(X,s) = e^{\frac{Pe}{2}X} C_i^{LV}(X,s) + \frac{c_{i,0}}{s} \tag{17}$$

Eqs. (14a), (14b), (15) and (16) are then written as

$$\frac{1}{Pe}\frac{d^2 C_1^{LV}(X,s)}{dX^2} - \left(\Theta_1(s) + \frac{Pe}{4}\right) C_1^{LV}(X,s) = \frac{c_{1,0}}{s}\Theta_1(s) e^{-\frac{Pe}{2}X} \tag{18a}$$

$$\begin{aligned} &\frac{1}{Pe}\frac{d^2 C_i^{LV}(X,s)}{dX^2} - \frac{dC_i^{LV}(X,s)}{dX} - \Theta_i(s) C_i^{LV}(X,s) \\ &= \frac{c_{i,0}}{s}\Theta_i(s) e^{-\frac{Pe}{2}X} - \Lambda_{i-1}\left(C_{i-1}^{LV}(X,s) + \frac{c_{i-1,0}}{s} e^{-\frac{Pe}{2}X} \right) \end{aligned} \tag{18b}$$

$$-\frac{dC_i^{LV}(X=0,s)}{dX} + \frac{Pe}{2} C_i^{LV}(X=0,s) = 0 \qquad i = 1,\ldots,N \tag{19}$$

$$\frac{dC_i^{LV}(X=1,s)}{dX} + \frac{Pe}{2} C_i^{LV}(X=1,s) = 0 \qquad i = 1,\ldots,N \tag{20}$$

The integral transform technique for eliminating the second-order spatial derivative with respect to X is dependent on the governing equations in Eqs. (18a) and (18b) and their corresponding boundary conditions in Eqs. (19) and (20). The appropriate integral transform pairs in relation to Eqs. (18a), (18b), (19) and (20) can be found as follows (Chen et al., 2012a):

$$G\left[C_i^{LV}(X,s)\right] = C_i^{LVG}(\psi_m,s) = \int_0^1 K(\psi_m,X) C_i^{LV}(X,s) dX \tag{21a}$$

$$G\left[C_i^{LVG}(X,s)\right] = C_i^{LV}(X,s) = \sum_{m=1}^{\infty} N(\psi_m) K(\psi_m,X) C_i^{LVG}(\psi_m,s) \tag{21b}$$

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where $K(\psi_m, X) = \frac{Pe}{2}\sin(\psi_m X) + \psi_m \cos(\psi_m X)$, $N(\psi_m) = \frac{2}{\frac{Pe^2}{4} + Pe + \psi_m{}^2}$, and ψ_m is the eigenvalue determined from the following equation

$$\psi_m \cot\psi_m - \frac{\psi_m{}^2}{Pe} + \frac{Pe}{4} = 0 .$$

The operational formula for the generalized integral transform of the second-order derivatives of $C_i{}^{LV}(X,s)$ satisfies

$$G\left[\frac{d^2 C_i{}^{LV}(X,s)}{dX^2}\right] = -\psi_m{}^2\left[C_i{}^{LV}(X,s)\right] \tag{22}$$

Taking the integral transform operator (Eq. (21a) on both sides of Eq. (18a) and we get

$$-\left(\Theta_1(s) + \frac{Pe}{4} + \frac{\psi_m{}^2}{Pe}\right) C_1{}^{LHV}(X,s) = \frac{c_{1,0}}{s}\Theta_1(s)\Phi(\psi_m) \tag{23a}$$

$$\begin{aligned} &-\left(\Theta_i(s) + \frac{Pe}{4} + \frac{\psi_m{}^2}{Pe}\right) C_i{}^{LVG}(X,s) \\ &= \frac{c_{i,0}}{s}\Theta_i(s)\Phi(\psi_m) - \Lambda_{i-1}\left(C_{i-1}{}^{LVG}(X,s) + \frac{c_{i-1,0}}{s}\Phi(\psi_m)\right) \end{aligned} \tag{23b}$$

where $\Phi(\psi_m) = \frac{Pe\,\psi_m}{\frac{Pe^2}{4} + \psi_m{}^2}$.

Solving Eqs. (23a) and (23b) for each individual species $C_i{}^{LVG}(\psi_m, s)$ in sequence, we can generalize $C_i{}^{LVG}(\psi_m, s)$ in a compact expression as

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$$C_i^{LVG}(X,s)=\left[-\frac{c_{i,0}}{s}\frac{\Theta_i(s)}{p_i(s)}+\sum_{l=1}^{l=i-1}\frac{c_{i-l,0}}{s}\frac{\left(\prod_{k=i-l}^{k=i-1}\Lambda_k\right)\left(p_{i-l}(s)-\Theta_{i-l}(s)\right)}{\prod_{k=i-l}^{k=i}p_k(s)}\right]\Phi(\psi_m) \quad (24)$$

where . $p_i(s)=\Theta_i(s)+\frac{Pe}{4}+\frac{{\psi_m}^2}{Pe}$.

3. Results and discussion

3.1 Convergence evaluation and verification of the derived analytical solution

The derived generalized analytical solution in Eq. (24) is mathematically expressed as the sum of an infinite series expansion. The numerical evaluation of this infinite series expansion sum can be calculated straightforwardly. To ensure the precision of the numerical evaluation, while at the same time avoiding the redundant computation of the infinite series expansion term by term, it is important to investigate the convergence behavior of the numerical evaluation of the derived analytical solutions. We executed routine convergence tests to determine the optimal number required for summing up the infinite series expansion term by term to obtain the desired accuracies. An illustrated example coming from the manual for the most commonly used public domain model BIOCHLOR provided by the Center for Subsurface Modeling Support of the United States Environmental Protection Agency (USEPA) (Aziz et al., 2000) is considered herein to evaluate the convergence of the numerical calculation of the developed analytical model. This illustrative example simulates the natural attenuation of the groundwater contaminant plumes of a chlorinated solvent site. The biodegradation pathway of the chlorinated solvent is assumed to follow sequential first-

order kinetics as follows: $PCE \rightarrow TCE \rightarrow DCE \rightarrow VC \rightarrow ETH$. The descriptive simulation conditions and transport parameters are summarized in Table 1. Table2 shows the convergence behavior obtained by the numerical evaluation of the spatial concentration profiles of the five species using the derived analytical solution in Eq. (24) with a desired accuracy of 2 decimal digits. In Table 2, *N* is defined as the number required for summing up the infinite series expansion term by term. It can be seen that for larger values of *Pe*, the evaluation must be carried out with a large number for summing up the series expansion to desired accuracy of 2 decimal digits. Moreover, the number required for accurately summing up the series expansion decreases as the serial number of the species increases. The number of terms required for convergence are 40, 1000 and 16,000 for *Pe*=1, 10 and 20, respectively, for the PCE of the first species, and 20, 320 and 2,000, respectively, for *Pe*=1, 10 and 20 for the TCE of the second species. For VC of the fourth species, convergence is reached when the numbers of terms are 8, 80 and 800 for *Pe*=1, 10 and 20, while for ETH only 8, 20 and 100 terms are required to meet the desired accuracy for *Pe* = 1, 10 and 20.

A computer code for executing the calculation of the developed analytical model is constructed based on the aforementioned convergence criterion. Comparison between the computed results obtained from the computer code constructed for the analytical model and the simulated results from a corresponding numerical solutions is carried out to assess the correctness the derived analytical model, as well as the accuracy of its auxiliary computer code. The numerical solutions are obtained using the Laplace transform finite difference (LTFD) method developed by Moridis and Reddel (1991) for the purpose of solving the partial differential equation for transient groundwater flow through porous media. The LTFD method provides an approach to

325 solve the discretized partial differential equation in the Laplace domain and then
326 numerically invert the transformed solution vectors. Therefore, we are able to obtain a
327 solution which is only discretized in space and continuous in time. The comparative
328 example considers the same simulation conditions and transport parameters for natural
329 attenuation of the contamination plumes of a chlorinated solvent site as those used for
330 the convergence evaluation. The comparison clearly shows excellent agreement
331 between the spatial concentration distributions for all five species obtained from the
332 analytical and numerical solutions (see supporting information). The results confirm
333 the correctness of the developed analytical models as well as the accuracy and
334 usefulness of the constructed computer code.
335
336 **3.2 Effect of the kinetic sorption rate constant (β_i)**
337 The major merit of the derived analytical solution is that the sorption process can
338 be more realistically and flexibly described as a first-order reversible kinetic sorption
339 process with an important kinetic sorption rate constant (β_i). Therefore, we are
340 interested in how β_i affects the multispecies plume migration. We now consider the
341 same multispecies transport problem used in the previous convergence evaluation and
342 solution verification to investigate the effect of β_i on multispecies plume
343 development. The simulation conditions and model parameters used in the convergence
344 tests are considered as a baseline simulation. For each of the individual species *i*, four
345 values of β_i (0, 0.5, 5 and 50 year^{-1}) are considered in order to investigate the effect
346 of β_i on multispecies transport. Figure 1 depicts the spatial concentration profiles of
347 the five species at *t*=1 year under different β_i values. The spatial concentration

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348 profiles of the five species obtained with the equilibrium-controlled linear sorption
349 model are also included in Fig. 1. It is found that an increase in β_i will lead to a
350 decrease in the peak concentration and a upstream shift in the location of the peak
351 concentration. As β_i continues to increase, the spatial concentration profile obtained
352 from the rate-limited sorption model of gradually reaches those obtained from the
353 equilibrium-controlled sorption model. The spatial concentration profiles show that the
354 rate-limited sorption model of β_i =50 year^{-1} coincides with the equilibrium-controlled
355 sorption model. It further demonstrates that the asymptotical condition of the rate-
356 limited sorption model agrees with the equilibrium-controlled sorption model. The
357 higher peak concentrations predicted by the rate-limited sorption model with small β_i
358 values have important implications for groundwater contaminant concentration
359 predictions as well as the assessment of the risk to human health. It should be noted that
360 the health risk might be underestimated when an equilibrium-controlled sorption model
361 is used for assessing the exposure concentration.

362 To measure the relative importance of rate-limited sorption between the dissolved
363 and sorbed phases in comparison to advection process, the sorption Damköler number,
364 $Da_i = \frac{\beta_i L}{v}$, which is the ratio of time ($\frac{L}{v}$) taken for the groundwater moving a distance
365 L through the aquifer to the time scale for kinetic sorption rate constant β_i is
366 considered. The Da_i is a dimensionless number to relate the sorption reaction rate to
367 the advective transport rate is considered. A smaller value of Da_i indicates that the
368 sorption reaction rate between the dissolved and the sorbed phase is relatively smaller
369 in comparison to rate of the groundwater flow through a porous medium. As β_i

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370 gradually increases, the Da_i increases proportionally. With coincidence between the
371 rate-limited sorption model of $\beta_i = 50y^{-1}$ and the equilibrium-controlled sorption
372 model, $Da_i = \frac{\beta_i L}{v} = \frac{50y^{-1} \times 330.7m}{34.0m/y} = 486.$ is obtained. It should be noted that
373 $Da_i = 486$ for validity condition of the equilibrium-controlled sorption model is
374 obtained on our descriptive simulation conditions and transport parameters. Uncertainty
375 analysis on the value for the threshold of Da should be conducted to support the general
376 validity condition. Nevertheless, considering the valid condition of the equilibrium-
377 controlled sorption model can vary with the combinations of all the transport
378 parameters used in the modeling process, the Damköler number greater than 2 to 3 order
379 of magnitude is suggested.
380 The results of the aforementioned investigation clearly evidence that the kinetic
381 sorption rate constant is an important parameter governing the multispecies plume
382 transport. However, because of the difficulty in obtaining the sorption reaction rate
383 constant, current transport modeling practices are often based on the equilibrium
384 sorption assumption. Thus, more efforts are required to develop a method for more
385 effective and accurately determining the kinetic sorption rate coefficient in the field
386
387 **3.3 Effect of inlet boundary condition**
388 Several previous studies have discussed the mass balance constraints and potential
389 errors in concentration prediction when improper inlet boundary conditions are used
390 for the development of the single-species transport analytical model (van Genuchten
391 and Parker, 1984; Leij et al., 1991, Chen et al., 2011a; 2011b). Single-species transport

analytical models with a first-type inlet condition give rise to physically improper mass conservation and significant errors in predicting the solute concentration distribution, especially for a porous medium system with a large longitudinal dispersion coefficient if it is used to interpret the usual volume-average concentration. Selection of the appropriate inlet boundary condition has been the subject of much investigation, such as for the study of solute transport either in a uniform flow ((van Genuchten and Parker, 1984; Leij et al., 1991; Chen et al. 2011a; 2011b) or a radial flow field (Chen, 1987). To the best of the author's knowledge, the effect of the inlet boundary condition on multispecies transport has not been investigated yet. Here, the impact of the inlet boundary conditions on multispecies transport are investigated using our derived multispecies transport analytical models subject to the first-type and third-type inlet boundary conditions. The analytical solutions for the-first-type inlet boundary condition can be obtained following the same method. Chen et al. (2011b) has showed how to obtain the analytical solution for single-species transport in a finite domain with a first-type inlet boundary condition. Figure 2 depicts the spatial concentration profiles of the five species at t=1 year for both the first-type and third-type inlet boundary conditions. using different dispersion coefficient values. It is observed that the predicted concentration is higher for the first-type inlet boundary condition than with the third-type inlet boundary condition for all species. Moreover, with an increasing dispersion coefficient, the discrepancy between the concentration distributions for first-type and third-type inlet boundary conditions increases along with the discrepancy between the peak concentrations. The results show that improper inlet boundary conditions leads to pronounced mass balance errors, and the discrepancy increases as the dispersion coefficient increases

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4. Conclusions

In this study, a novel analytical model is developed for multispecies advective-dispersive transport subject to rate-limited sorption. The developed model is then applied to assess the effects of the kinetic sorption rate constant on multispecies transport. Increasing the kinetic sorption rate constant leads to lower concentration predictions for all species of the degradable contaminants. The equilibrium-controlled sorption model could significantly underestimate the concentration of decaying or degradable contaminants under the condition of a low sorption Damköler number, $Da_i = \frac{\beta_i L}{v}$, but will agrees well with the rate-limited sorption model when the sorption Damköler number is greater than 486. It should be noted that $Da_i = 486$ for validity condition of the equilibrium-controlled sorption model is obtained on our descriptive simulation conditions and transport parameters. Uncertainty analysis on the value for the threshold of Da should be conducted to support the general validity condition. The invalidity of the equilibrium-controlled sorption model under a low sorption Damköler number suggests that the health risk might be underestimated when an equilibrium-controlled sorption model is used for assessing the exposure concentration in the health risk assessment of the contaminated site.

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607 **Table 1. The descriptive simulation conditions and transport parameters**

Parameter	Value
Domain length, L [m]	330.7
Seepage velocity, v [m year^{-1}]	34.0
Dispersion coefficient, D [m^2 year^{-1}]	1,000
Bulk dry density of the solid grain, ρ_b [kg L^{-1}]	1.6
Effective porosity, θ [-]	0.2
Distribution coefficient, K_i [L kg^{-1}]	
PCE	0.784
TCE	0.239
DCE	0.230
VC	0.0545
ETH	0.556
Retardation factor, R_i [-]	
PCE	7.27
TCE	2.91
DCE	2.84
VC	1.44
ETH	5.45
Sorption reaction rate constant, β_i [year^{-1}]	
PCE	0.5
TCE	0.5
DCE	0.5
VC	0.5
ETH	0.5
Decay constant, λ_i [year^{-1}]	
PCE	2
TCE	1
DCE	0.7
VC	0.4
ETH	0
Source concentration, $c_{i,0}$ [mg/L]	
PCE	0.056
TCE	15.8
DCE	98.5
VC	3.080
ETH	0.030

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Table 2. The convergence behaviors from numerical evaluation of the spatial concentration distributions of the five species for biodegradation of a chlorinated solvent at t= 10 years using the derived analytical solution. (M = number of terms summed for infinite series expansion).

PCE				
Pe=1				
x [m]	N=10	N=20	N=40	N=80
0	1.15×10^{-2}	1.15×10^{-2}	1.15×10^{-2}	1.15×10^{-2}
82.7	3.88×10^{-3}	3.88×10^{-3}	3.89×10^{-3}	3.89×10^{-3}
165.3	1.31×10^{-3}	1.32×10^{-3}	1.32×10^{-3}	1.32×10^{-3}
248	4.71×10^{-4}	4.70×10^{-4}	4.70×10^{-4}	4.70×10^{-4}
330.7	2.69×10^{-4}	2.66×10^{-4}	2.66×10^{-4}	2.66×10^{-4}
Pe=10				
x [m]	N=250	N=500	N=1,000	N=2,000
0	2.86×10^{-2}	2.86×10^{-2}	2.86×10^{-2}	2.86×10^{-2}
82.7	1.92×10^{-3}	1.92×10^{-3}	1.92×10^{-3}	1.92×10^{-3}
165.3	1.27×10^{-4}	1.27×10^{-4}	1.27×10^{-4}	1.27×10^{-4}
248	8.38×10^{-6}	8.37×10^{-6}	8.37×10^{-6}	8.37×10^{-6}
330.7	9.22×10^{-7}	8.20×10^{-7}	8.13×10^{-7}	8.13×10^{-7}
Pe=20				
x [m]	N=4,000	N=8,000	N=16,000	N=32,000
0	3.52×10^{-2}	3.52×10^{-2}	3.52×10^{-2}	3.52×10^{-2}
82.7	1.26×10^{-3}	1.26×10^{-3}	1.26×10^{-3}	1.26×10^{-3}
165.3	4.43×10^{-5}	4.43×10^{-5}	4.43×10^{-5}	4.43×10^{-5}
248	1.53×10^{-6}	1.53×10^{-6}	1.53×10^{-6}	1.53×10^{-6}
330.7	7.30×10^{-8}	7.13×10^{-8}	7.12×10^{-8}	7.12×10^{-8}

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TCE				
Pe=1				
x [m]	*N*=5	*N*=10	*N*=20	*N*=40
0	4.41×10^{0}	4.40×10^{0}	4.40×10^{0}	4.40×10^{0}
82.7	2.12×10^{0}	2.12×10^{0}	2.12×10^{0}	2.12×10^{0}
165.3	1.03×10^{0}	1.03×10^{0}	1.03×10^{0}	1.03×10^{0}
248	5.47×10^{-1}	5.41×10^{-1}	5.41×10^{-1}	5.41×10^{-1}
330.7	3.87×10^{-1}	3.95×10^{-1}	3.94×10^{-1}	3.94×10^{-1}
Pe=10				
x [m]	*N*=80	*N*=160	*N*=320	*N*=640
0	9.96×10^{0}	9.96×10^{0}	9.96×10^{0}	9.96×10^{0}
82.7	1.88×10^{0}	1.88×10^{0}	1.88×10^{0}	1.88×10^{0}
165.3	3.42×10^{-1}	3.42×10^{-1}	3.42×10^{-1}	3.42×10^{-1}
248	6.04×10^{-2}	6.00×10^{-2}	6.00×10^{-2}	6.00×10^{-2}
330.7	1.55×10^{-2}	1.42×10^{-2}	1.40×10^{-2}	1.40×10^{-2}
Pe=20				
x [m]	*N*=500	*N*=1,000	*N*=2,000	*N*=4,000
0	1.17×10^{1}	1.17×10^{1}	1.17×10^{1}	1.17×10^{1}
82.7	1.64×10^{0}	1.64×10^{0}	1.64×10^{0}	1.64×10^{0}
165.3	2.15×10^{-1}	2.15×10^{-1}	2.15×10^{-1}	2.15×10^{-1}
248	2.64×10^{-2}	2.64×10^{-2}	2.64×10^{-2}	2.64×10^{-2}
330.7	4.93×10^{-3}	3.96×10^{-3}	3.89×10^{-3}	3.89×10^{-3}

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DCE				
Pe=1				
x [m]	*N*=4	*N*=8	*N*=16	*N*=32
0	3.35×10^{1}	3.34×10^{1}	3.34×10^{1}	3.34×10^{1}
82.7	1.91×10^{1}	1.92×10^{1}	1.92×10^{1}	1.92×10^{1}
165.3	1.12×10^{1}	1.11×10^{1}	1.11×10^{1}	1.11×10^{1}
248	6.84×10^{0}	6.91×10^{0}	6.90×10^{0}	6.90×10^{0}
330.7	5.61×10^{0}	5.54×10^{0}	5.54×10^{0}	5.54×10^{0}
Pe=10				
x [m]	*N*=40	*N*=80	*N*=160	*N*=320
0	7.03×10^{1}	7.03×10^{1}	7.03×10^{1}	7.03×10^{1}
82.7	2.14×10^{1}	2.14×10^{1}	2.14×10^{1}	2.14×10^{1}
165.3	5.93×10^{0}	5.93×10^{0}	5.93×10^{0}	5.93×10^{0}
248	1.55×10^{0}	1.53×10^{0}	1.53×10^{0}	1.53×10^{0}
330.7	5.76×10^{-1}	4.97×10^{-1}	4.92×10^{-1}	4.92×10^{-1}
Pe=20				
x [m]	*N*=250	*N*=500	*N*=1,000	*N*=2,000
0	8.03×10^{1}	8.03×10^{1}	8.03×10^{1}	8.03×10^{1}
82.7	2.05×10^{1}	2.05×10^{1}	2.05×10^{1}	2.05×10^{1}
165.3	4.54×10^{0}	4.54×10^{0}	4.54×10^{0}	4.54×10^{0}
248	8.96×10^{-1}	8.94×10^{-1}	8.94×10^{-1}	8.94×10^{-1}
330.7	2.55×10^{-1}	2.00×10^{-1}	1.96×10^{-1}	1.96×10^{-1}

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VC				
Pe=1				
x [m]	*N*=2	*N*=4	*N*=8	*N*=16
0	1.86×10^{1}	1.94×10^{1}	1.96×10^{1}	1.96×10^{1}
82.7	2.11×10^{1}	2.10×10^{1}	2.09×10^{1}	2.09×10^{1}
165.3	1.97×10^{1}	1.88×10^{1}	1.89×10^{1}	1.89×10^{1}
248	1.63×10^{1}	1.66×10^{1}	1.65×10^{1}	1.65×10^{1}
330.7	1.45×10^{1}	1.54×10^{1}	1.55×10^{1}	1.55×10^{1}
Pe=10				
x [m]	*N*=20	*N*=40	*N*=80	*N*=160
0	2.19×10^{1}	2.19×10^{1}	2.20×10^{1}	2.20×10^{1}
82.7	3.57×10^{1}	3.56×10^{1}	3.56×10^{1}	3.56×10^{1}
165.3	2.21×10^{1}	2.22×10^{1}	2.22×10^{1}	2.22×10^{1}
248	1.09×10^{1}	1.05×10^{1}	1.06×10^{1}	1.06×10^{1}
330.7	3.80×10^{1}	5.22×10^{1}	5.31×10^{1}	5.31×10^{1}
Pe=20				
x [m]	*N*=200	*N*=400	*N*=800	*N*=1,600
0	1.79×10^{1}	1.79×10^{1}	1.79×10^{1}	1.79×10^{1}
82.7	3.95×10^{1}	3.95×10^{1}	3.95×10^{1}	3.95×10^{1}
165.3	2.23×10^{1}	2.23×10^{1}	2.23×10^{1}	2.23×10^{1}
248	8.93×10^{0}	8.94×10^{0}	8.94×10^{0}	8.94×10^{0}
330.7	3.12×10^{0}	3.27×10^{0}	3.28×10^{0}	3.28×10^{0}

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Pe=1				
x [m]	*N*=2	*N*=4	*N*=8	*N*=16
0	1.48×10^{1}	1.49×10^{1}	1.49×10^{1}	1.49×10^{1}
82.7	1.82×10^{1}	1.82×10^{1}	1.82×10^{1}	1.82×10^{1}
165.3	2.00×10^{1}	1.99×10^{1}	1.99×10^{1}	1.99×10^{1}
248	2.05×10^{1}	2.06×10^{1}	2.05×10^{1}	2.05×10^{1}
330.7	2.05×10^{1}	2.07×10^{1}	2.07×10^{1}	2.07×10^{1}
Pe=10				
x [m]	*N*=5	*N*=10	*N*=20	*N*=40
0	7.49×10^{0}	7.84×10^{0}	7.87×10^{0}	7.87×10^{0}
82.7	2.82×10^{1}	2.78×10^{1}	2.78×10^{1}	2.78×10^{1}
165.3	3.31×10^{1}	3.20×10^{1}	3.19×10^{1}	3.19×10^{1}
248	1.56×10^{1}	2.44×10^{1}	2.46×10^{1}	2.46×10^{1}
330.7	5.19×10^{1}	1.59×10^{1}	1.73×10^{1}	1.73×10^{1}
Pe=20				
x [m]	*N*=25	*N*=50	*N*=100	*N*=200
0	4.11×10^{0}	4.12×10^{0}	4.12×10^{0}	4.12×10^{0}
82.7	3.01×10^{1}	3.01×10^{1}	3.01×10^{1}	3.01×10^{1}
165.3	3.62×10^{1}	3.62×10^{1}	3.62×10^{1}	3.62×10^{1}
248	2.73×10^{1}	2.59×10^{1}	2.60×10^{1}	2.60×10^{1}
330.7	3.58×10^{1}	1.38×10^{1}	1.47×10^{1}	1.47×10^{1}

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Figure Captions

Figure 1. Effect of the sorption rate constant on the spatial concentration distribution of species1 at t=1 day obtained from the derived rate-limited sorption model. The solid lines are the results from the rate-limited model and the circles represent the results from the equilibrium-controlled sorption model

Figure 2. Effect of the inlet boundary conditions on the spatial concentration distribution of species1 at t=1 day using different dispersion coefficients.

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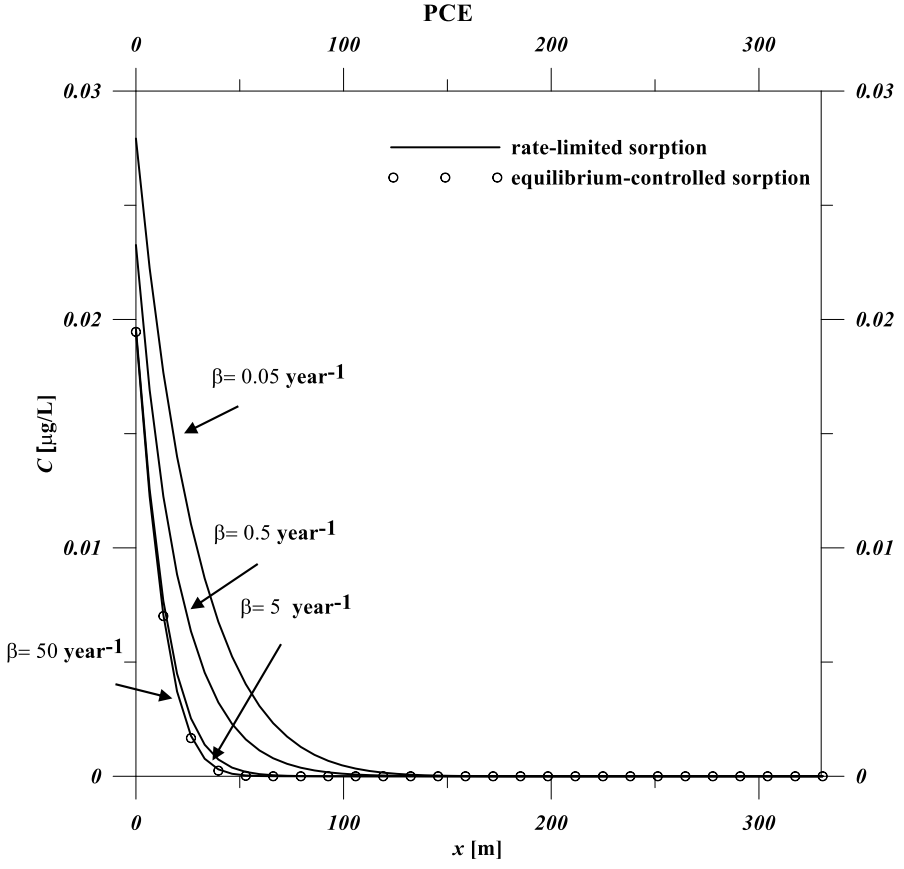

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711 **(a)**
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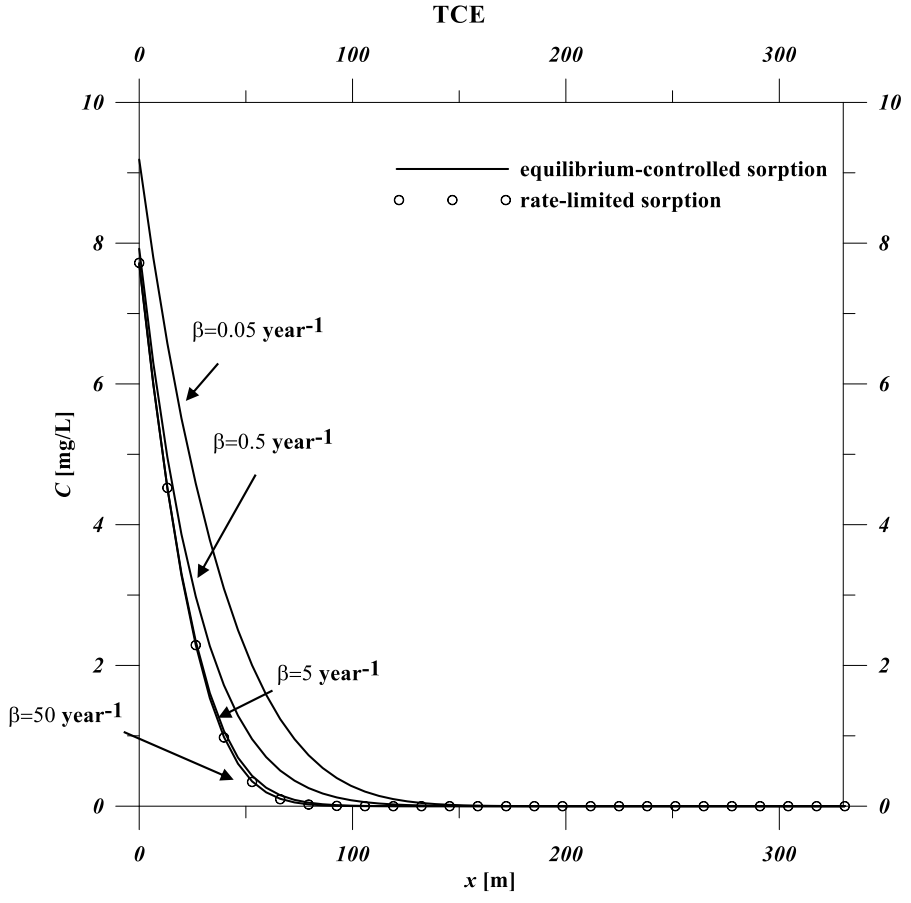

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726 **(b)**
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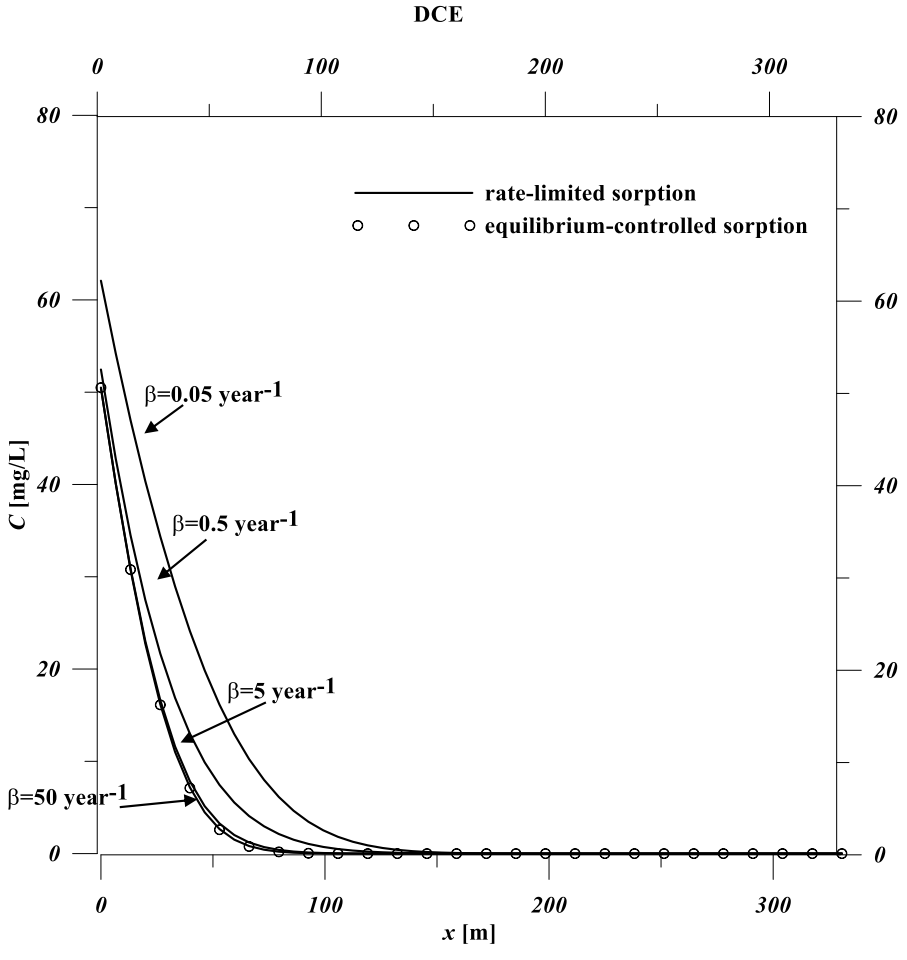

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740 **(c)**

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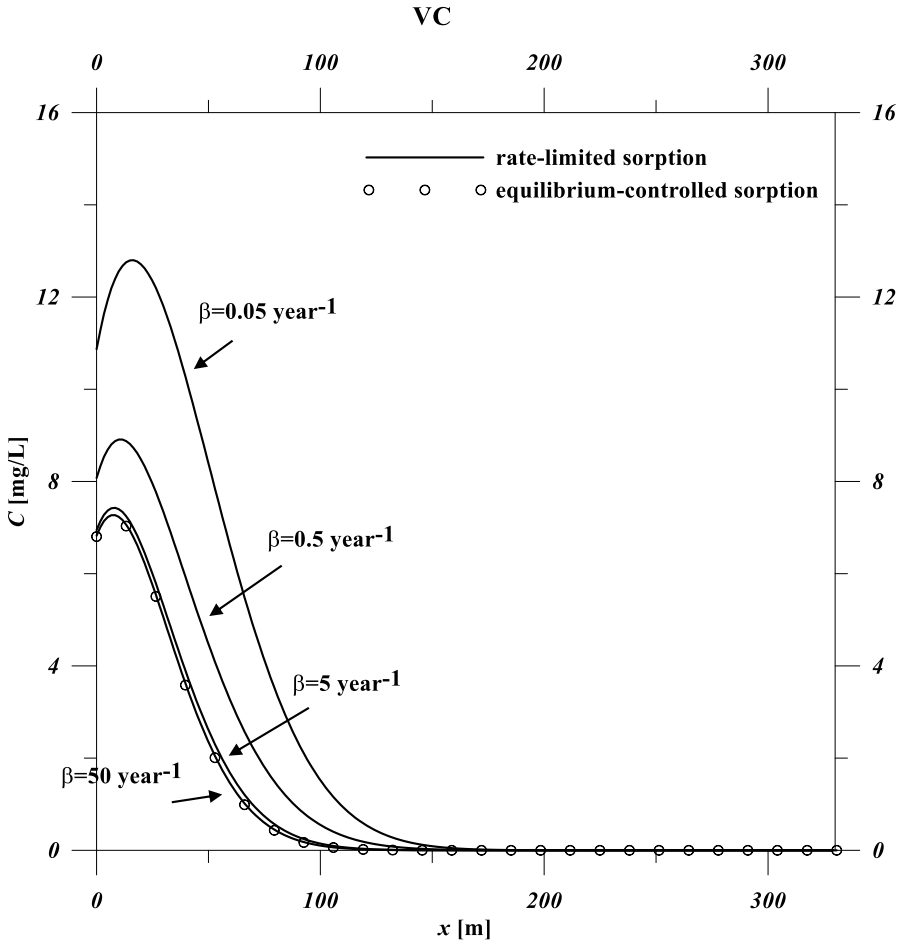

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753 **(d)**
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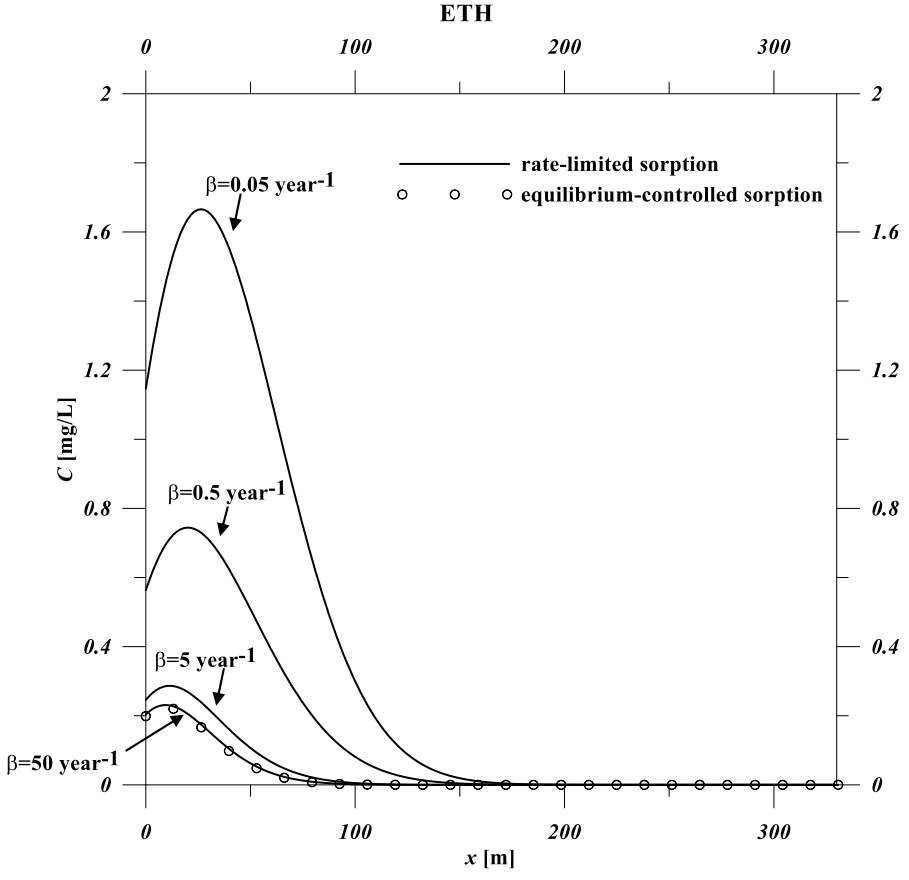
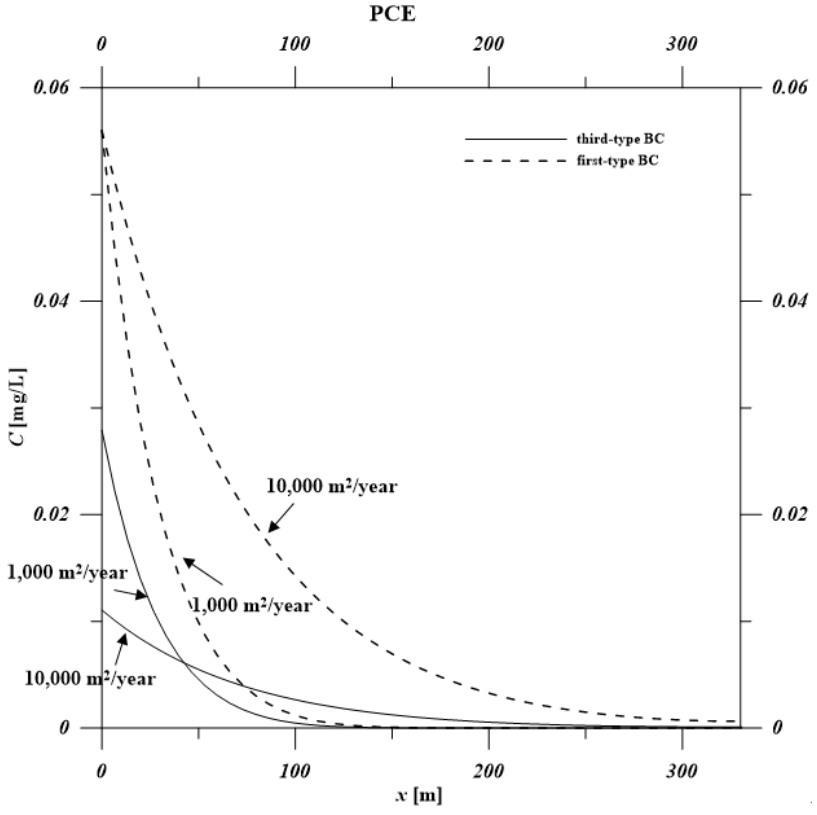


(e)

Fig. 1



(a)

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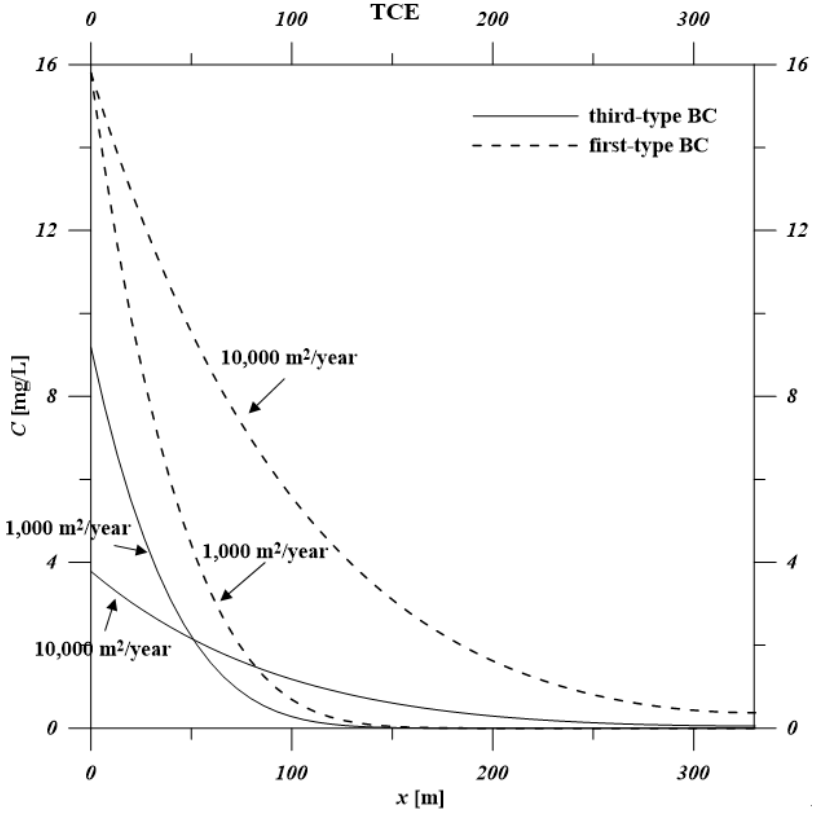

(b)

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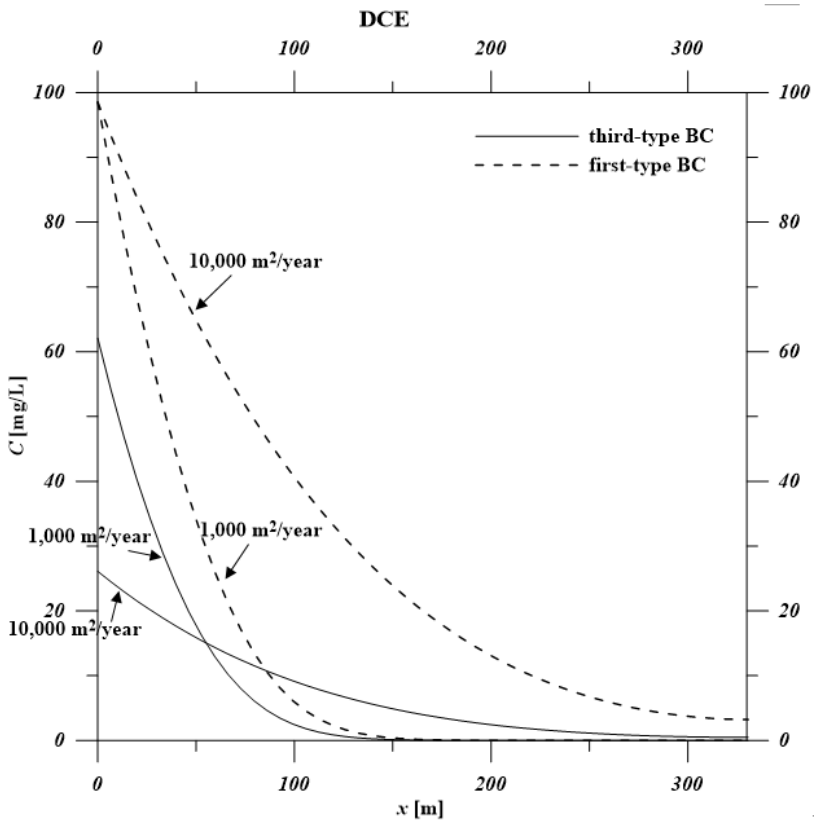

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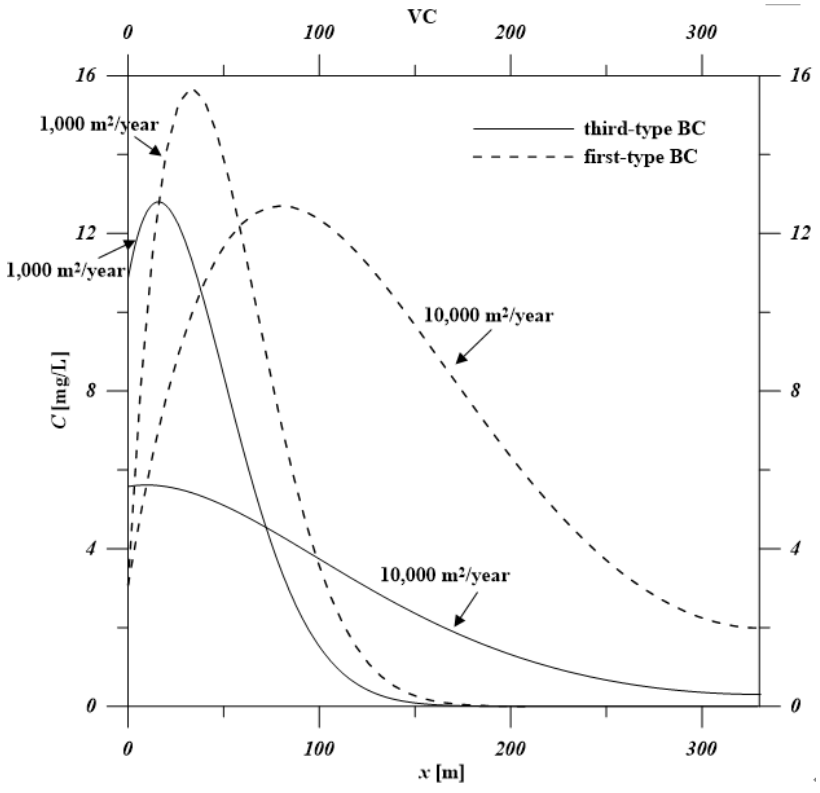

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818 **(d)**

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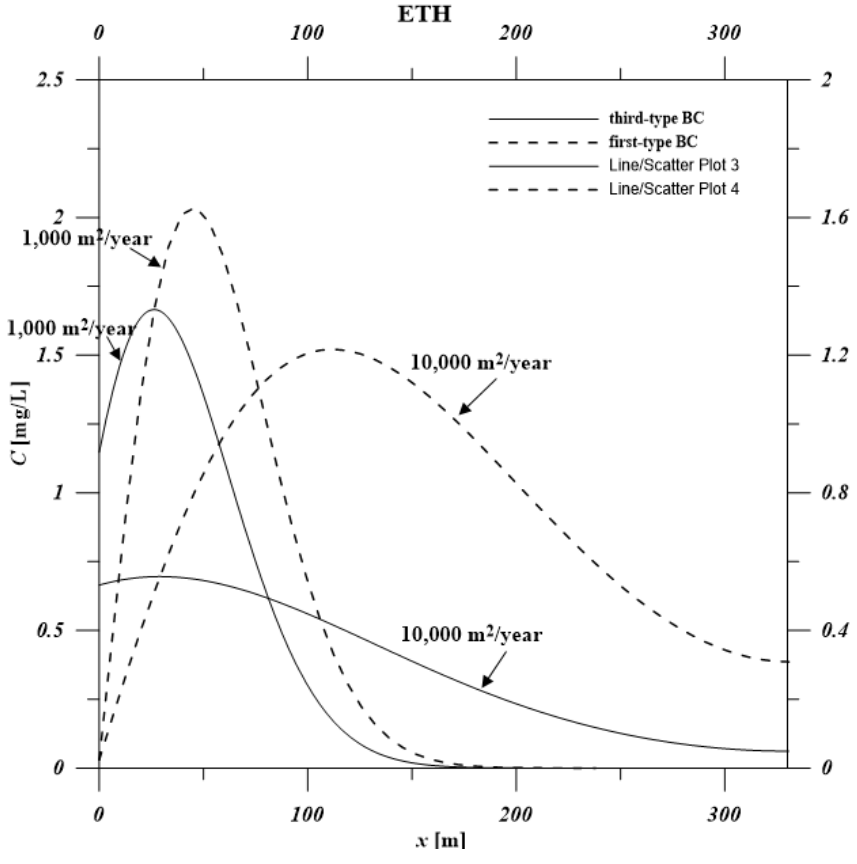

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829 **(e)**

830 **Fig. 2**

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