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

MING CUI* AND YAZHU DENG

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

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

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

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

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

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

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

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

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

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