Application of an Improved Mixing Cell Model to Equilibrium and Nonequilibrium Multispecies Transport

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1. Introduction

The mixing cell concept has been used frequently in the prediction of migration of reactive and non-reactive solutes in soil and groundwater (e.g., [1, 2, 3, 4, 5]). Mixing cell models are easy to code and efficient to compute and can be easily coupled with chemical speciation models to simulate complex reactions during transport. Mixing cell schemes are basically explicit finite difference representations of the governing transport equation. For tracer solutes, the mixing cell model is second-order accurate in the space and time discretization. It has been shown that the inclusion of a nonlinear adsorption isotherm in the transport equation reduces the accuracy of the standard mixing cell model [6]. We use here an improved mixing cell model which maintains second-order accuracy.

There are two types of predictive model used to analyse solute reaction rates during transport [7]. In one, the reaction is sufficiently fast to be described by an equilibrium model while for the other type, the reaction is relatively slow and is quantified by a nonequilibrium model. The main purpose of this study is to show the use of the improved mixing cell model in solving the transport of multispecies solutes undergoing either equilibrium or nonequilibrium reactions. The applicability of the numerical model is tested by simulating the field data of [8], corresponding to heterovalent exchange reactions involving three species.

2. Governing Equations

The governing equations for the multispecies equilibrium and nonequilibrium models are described below.

2.1. Multispecies Equilibrium Model. If the only reaction taking place is adsorption or ion exchange then, for a one-dimensional homogeneous soil column, the basic equations describing the transport of n reacting species can be expressed as (e.g., [9])

$$\frac{\partial\left[\frac{\rho S_k}{\theta} + C_k\right]}{\partial t} = D_s \frac{\partial^2 C_k}{\partial z^2} - V \frac{\partial C_k}{\partial z}, \quad k = 1, 2, \ldots, n. \tag{2.1}$$

Parameter meanings are collected in the Notation list. To solve the n equations in (2.1), an additional n equations defining the S_k functions are required. These equations are obtained from the chemical reaction laws describing the ion exchange process or other surface reaction laws, depending upon the type of reactions considered. For example, if only ion exchange is considered, then among the n exchanging

ions in the system, there are (n-1) independent equilibrium expressions of the form (e.g., [8]):

$$K_{lk} = \left(\frac{S_l*}{C_l}\right)^{\nu_k} \left(\frac{C_k}{S_k*}\right)^{\nu_l},\tag{2.2}$$

where

$$S_k* = \frac{S_k}{CEC} \quad k = 1, 2, \ldots, n.\tag{2.3}$$

The additional equation provided by the cation exchange capacity (CEC) is

$$CEC = \sum_{k=1}^{n} S_k.\tag{2.4}$$

Equations (2.2) and (2.4) when combined result in the n multispecies exchange isotherms:

$$S_k = f_k\Big(C_1, C_2, \ldots, C_n\Big), \quad k = 1, 2, \ldots, n.\tag{2.5}$$

Equations (2.1) and (2.5) constitute the basic multispecies equilibrium transport model.

2.2. Multispecies Nonequilibrium Model. When the reaction rates are not sufficiently rapid, an additional nonequilibrium equation given by (e.g., [10, 11])

$$\frac{\partial S_k}{\partial t} = \alpha_k\Big[f_k\Big(C_1, C_2, \ldots, C_n\Big) - S_k\Big], \quad k = 1, 2, \ldots, n.\tag{2.6}$$

is needed. Equations (2.1) and (2.6) constitute the nonequilibrium multispecies transport model. Note that S_k in this case is not the equilibrium concentration. Equation (2.6) states that when α_k is very large, the kth reaction approaches equilibrium and when α_k is 0, there is no reaction of that species at all.

We specify initial and boundary conditions that correspond to a step function input at the boundary z = 0

$$C_k\Big(z, 0\Big) = C_{kn}, \qquad z \geq 0,$$
$$C_k\Big(0, t\Big) = C_{kf}, \qquad t \geq 0.\tag{2.7}$$

The system of nonlinear equations (2.1) and (2.5) or (2.1) and (2.6) with initial and boundary conditions (2.7) are here solved by improved mixing cell model, described below.

2.3. Mixing Cell Model. Upon dropping second derivative term in the advective dispersive equation, (2.1), one gets the pure advective transport equation

$$\frac{\partial\left[\frac{\rho S_k}{\theta} + C_k\right]}{\partial t} = -V\frac{\partial C_k}{\partial z}, \quad k = 1, 2, \ldots, n. \tag{2.8}$$

Finite-difference solutions of (2.8) produce numerical dispersion which is controlled to simulate solutions to (2.1).

2.4. Improved Mixing Cell Model. The standard mixing cell has a first-order truncation error of $O(\Delta z^2, \Delta t)$ [6] and the following more accurate, second-order scheme is applied. The improved scheme is

$$\left(1 + \frac{C_r}{2}\right)C_k(i, j+1) + \frac{\rho}{\theta}S_k(i, j+1) = C_k(i, j) + \frac{\rho}{\theta}S_k(i, j)$$

$$+ \frac{C_r}{2}\left[C_k(i-1, j+1) + C_k(i-1, j) - C_k(i, j)\right], k = 1, 2, \ldots, n, \tag{2.9}$$

where $C_k(z, t) = C_k(i\Delta z, j\Delta t) = C_k(i, j)$, and C_r is the Courant number. At equilibrium, the solid phase concentration is:

$$S_k(i, j+1) = f_k\left[C_1(i, j+1), C_2(i, j+1), \ldots, C_n(i, j+1)\right], k = 1, 2, \ldots, n. \tag{2.10}$$

When (2.10) is used, (2.9) reduces to a set of n nonlinear equations in $C_k(i, j+1)$ which can be solved numerically. Note that (2.9) is written in terms of only j and $j+1$ time levels, so that initial and boundary conditions, (2.7) can be imposed. Because no exit condition can be imposed, it is evident that the solution will approximate that for a semi-infinite medium. To obtain results below, the nonlinear system of equations was solved by Newton's method. The Jacobian was determined by the finite difference method.

The truncation error of (2.9) is $O(\Delta z\Delta t, \Delta z^2, \Delta t^2)$ [6]. In this scheme the numerical dispersion introduced is $V\Delta z/2$. When the advective transport equations are to be solved by equation (2.9), the relation $D_s = V\Delta z/2$ is imposed, thus fixing the step length in the numerical scheme. The scheme is unconditionally stable. On the other hand, the standard scheme is $O(\Delta z^2, \Delta t)$ accurate and is conditionally stable [6]. In addition, the spatial and temporal steps in the standard scheme cannot be independently fixed as in the improved scheme. For the case of nonequilibrium exchange, the finite difference form of equation (2.6) is

$$\left(1 + \frac{\alpha_k\Delta t}{2}\right)S_k(i, j+1) = \frac{\alpha_k\Delta t}{2}\left[f_k\left(C_1(i, j+1), C_2(i, j+1), \ldots, C_n(i, j+1)\right)\right.$$

$$\left. + f_k\left(C_1(i, j), C_2(i, j), \ldots, C_n(i, j)\right) - S_k(i, j)\right] + S_k(i, j), k = 1, 2, \ldots, n. \tag{2.11}$$

Equations (2.9) and (2.11) with initial and boundary conditions (2.7) constitute the improved mixing cell solution of the multispecies nonequilibrium exchange reaction. Upon elimination of $S_k(i, j + 1)$, the combination of (2.9) and (2.11) again reduces the problem to that of n nonlinear equations unknown in $C_k(i, j + 1)$.

3. Comparison with a Crank-Nicolson scheme

The Crank-Nicolson scheme, which is second-order accurate, is a common way to solve transport equation (2.1) numerically. The set of nonlinear equations resulting from the application of the method is solved by iteration. Examples of both equilibrium and nonequilibrium reactions are considered here.

3.1. Equilibrium Reaction. The problem considered here is equation (2.1) with initial and boundary conditions equation (2.7) with the exchange isotherm given by equation (2.2). We consider bisolute homovalent exchange where the total sum of exchangeable ions in the feed and the native solutions are different. Observe that when the total sum of exchangeable ions in the feed and native solutions are equal, the problem reduces to a single species exchange problem. In the example shown in Figure 1, the total feed concentration was 10 $meq\,l^{-1}$ and that in the native solution was 100 $meq\,l^{-1}$. The concentration of species one in the feed concentration was assumed to be 9.5 $meq\,l^{-1}$ and that in the native solution to be 20 $meq\,l^{-1}$. The bulk density and porosity of the medium was assumed to be respectively 2 $g\,l^{-1}$ and 0.33 (e.g., [8]). The selectivity coefficient, k_{12} was taken to be unity. The concentration profiles for species one was generated at the dimensionless time of $V^2 t/D_s = 49.33$ by both mixing cell and Crank-Nicolson methods. The simulations were for a column Peclet number of 106.96. It is observed that mixing cell solutions are in excellent agreement with the Crank-Nicolson scheme.

3.2. Nonequilibrium Reaction. We next consider the case of a nonequilibrium situation for a bisolute homovalent exchange. As an illustrative example, the same constants as above were used with the rate parameter, α, set to 0.01 hr^{-1}. The profiles were generated at a dimensionless time of 49.33 as above by using both methods. Observe in Figure 2 that the mixing cell solutions again are in excellent agreement with the Crank-Nicolson.

4. Application to a field experiment

The field experiment reported by [8] consisted of injection of treated municipal wastewater effluent into an aquifer with known initial water composition. The species monitored were Ca, Mg and Na. The flow was radially outward from the injection well. The main chemical mechanism assumed to affect transport is ion exchange between the three species. The initial composition of groundwater at the injection point and the observation point are shown in Table 1. Also shown in the table is the composition of the injection water. The aquifer thickness, the bulk density of the soil matrix, the cation exchange capacity and the porosity were, respectively, 2 m, 1875 $g\,l^{-1}$, 0.1 $meq\,g^{-1}$, and 0.25. The selectivity coefficients k_{21} and k_{31} were 1.7 and 3.0 $eq\,l^{-1}$, respectively. Although the flow was radial, a constant average velocity was

assumed. The average pore water velocity as obtained from the chloride breakthrough curve of [8] is $1.12\ m\,hr^{-1}$. A dispersivity of $1.6\ m$ was used in the simulation. The spatial step required by the improved mixing cell model is $3.2\ m$. The simulations are shown in Figure 3 and 4 for Mg^{+2} and Ca^{+2} respectively. We observe that the mixing cell predictions are in excellent agreement with the experimental field results.

5. Summary and Conclusions

In ion exchange experiments, breakthrough curves or concentration profiles within the soil depict complex shapes characterised by plateaus and depressions. Since the soil and chemical properties are fixed, these features are dependent simply on the native and feed solute concentrations. A simple efficient improved mixing cell model has been applied to describe the concentration profiles. It is found that the results are in excellent agreement with those of a standard Crank-Nicolson scheme and, at the same time, the improved method is much easier to code and is faster to compute. The case of ternary heterovalent exchange of Na by Mg and Ca in a field experiment has been efficiently described by this method with simple assumptions like constant velocity and constant dispersivity.

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Notation

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C_k	liquid phase concentration of species k, ML^{-3}
C_{kf}	feed liquid phase concentration of species k, ML^{-3}
C_{kn}	native liquid phase concentration of species k, ML^{-3}
C_r	Courant number, $V\Delta t/\Delta z$
D_s	dispersion coefficient, L^2T^{-1}
$f_k(C)$	function of C
K_{lk}	selectivity coefficient
S_k	solid phase concentration of species k
t	time, T
V	mean pore water velocity, LT^{-1}
z	distance below soil surface, L
θ	porosity
ν_k	constant used in equation 2
ρ	bulk density, ML^{-3}
α_k	rate constant, T^{-1}
Δt	time step, T
Δz	spatial step, L
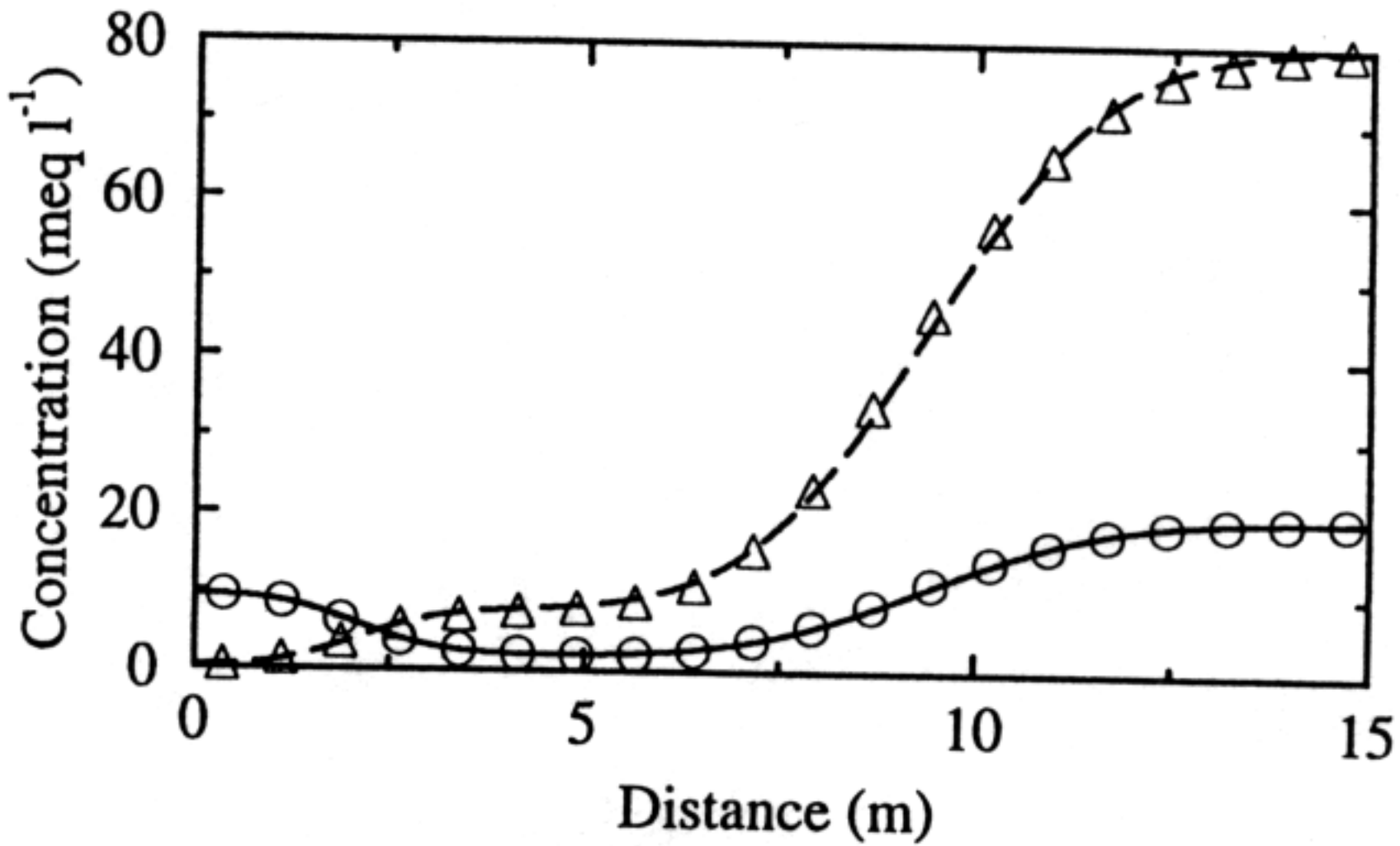
FIGURE 1. Comparison of mixing cell (circle is species 1 and triangle is species 2) and Crank-Nicolson (line is species 1 and dashes are species 2) solutions for nonlinear equilibrium transport.
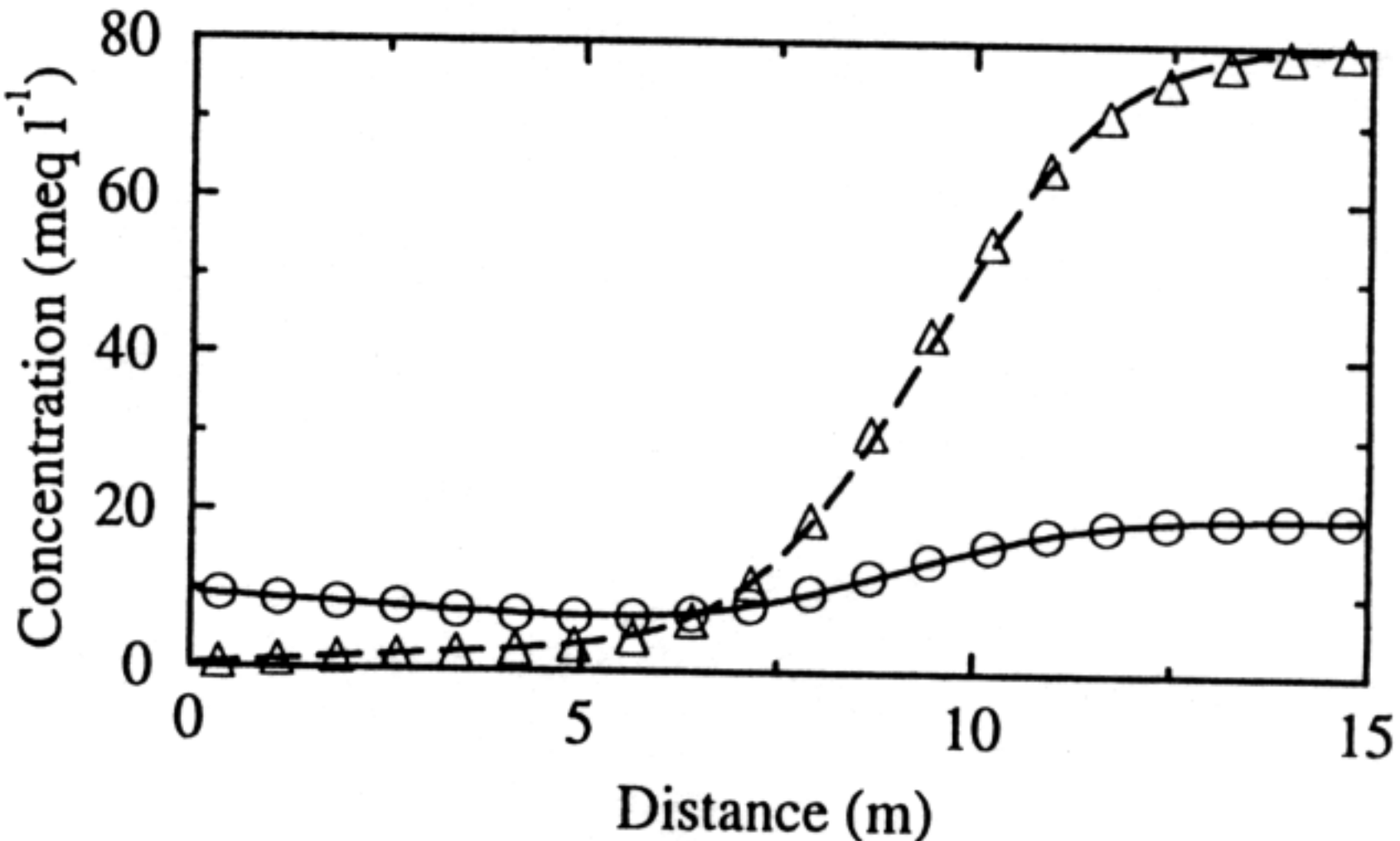

FIGURE 2. Comparison of mixing cell (circle is species 1 and triangle is species 2) and Crank-Nicolson (line is species 1 and dashes are species 2) solutions for nonlinear nonequilibrium transport.

TABLE 1. Composition of Feed and Native Water (All units are in $mg\,l^{-1}$)

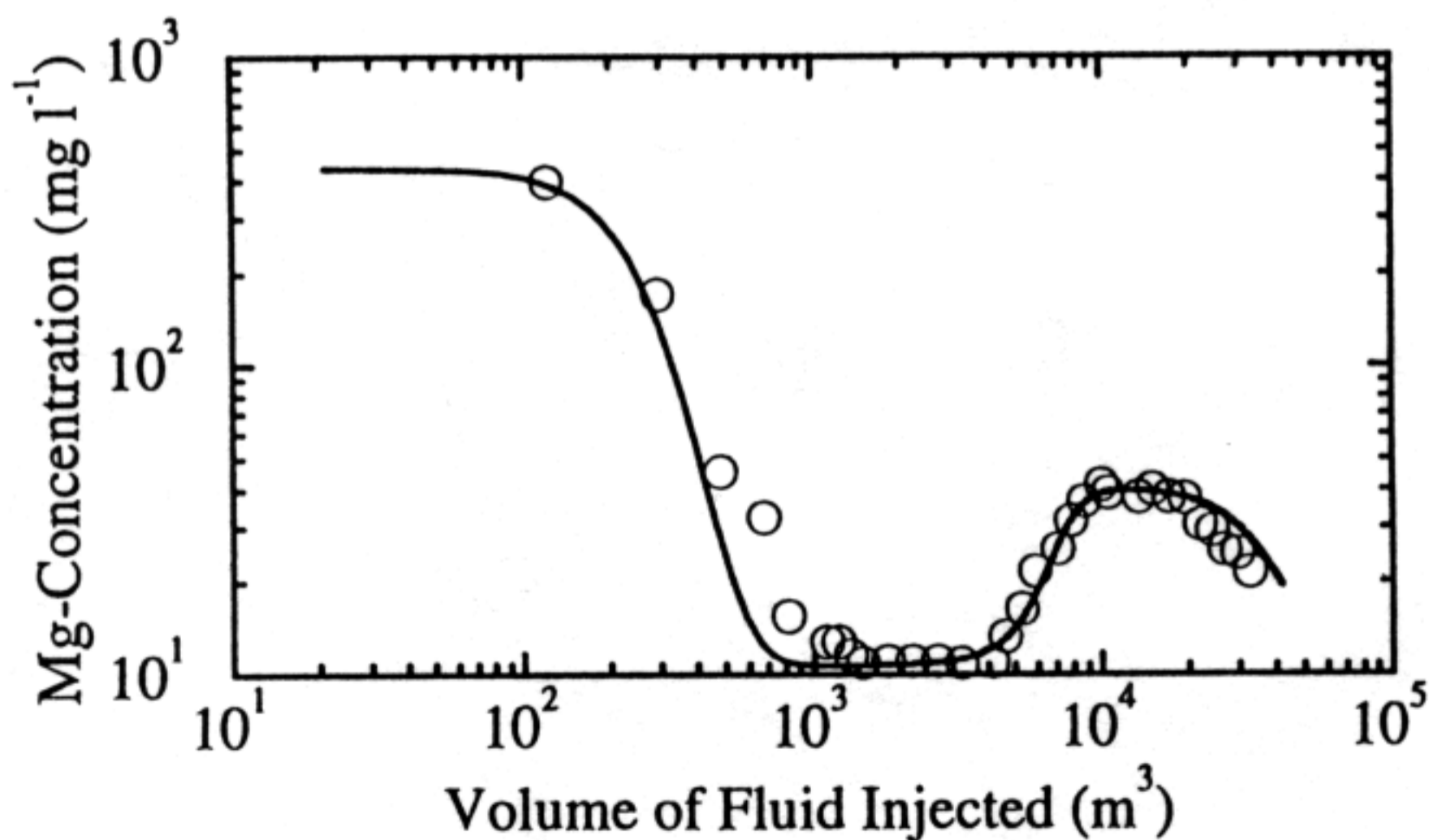| Species	Injection Water Feed water	Native Groundwater Injection Well	Observation Well
Na^+	216	1200	1990
Mg^{+2}	12	310	436
Ca^{+2}	85	262	444

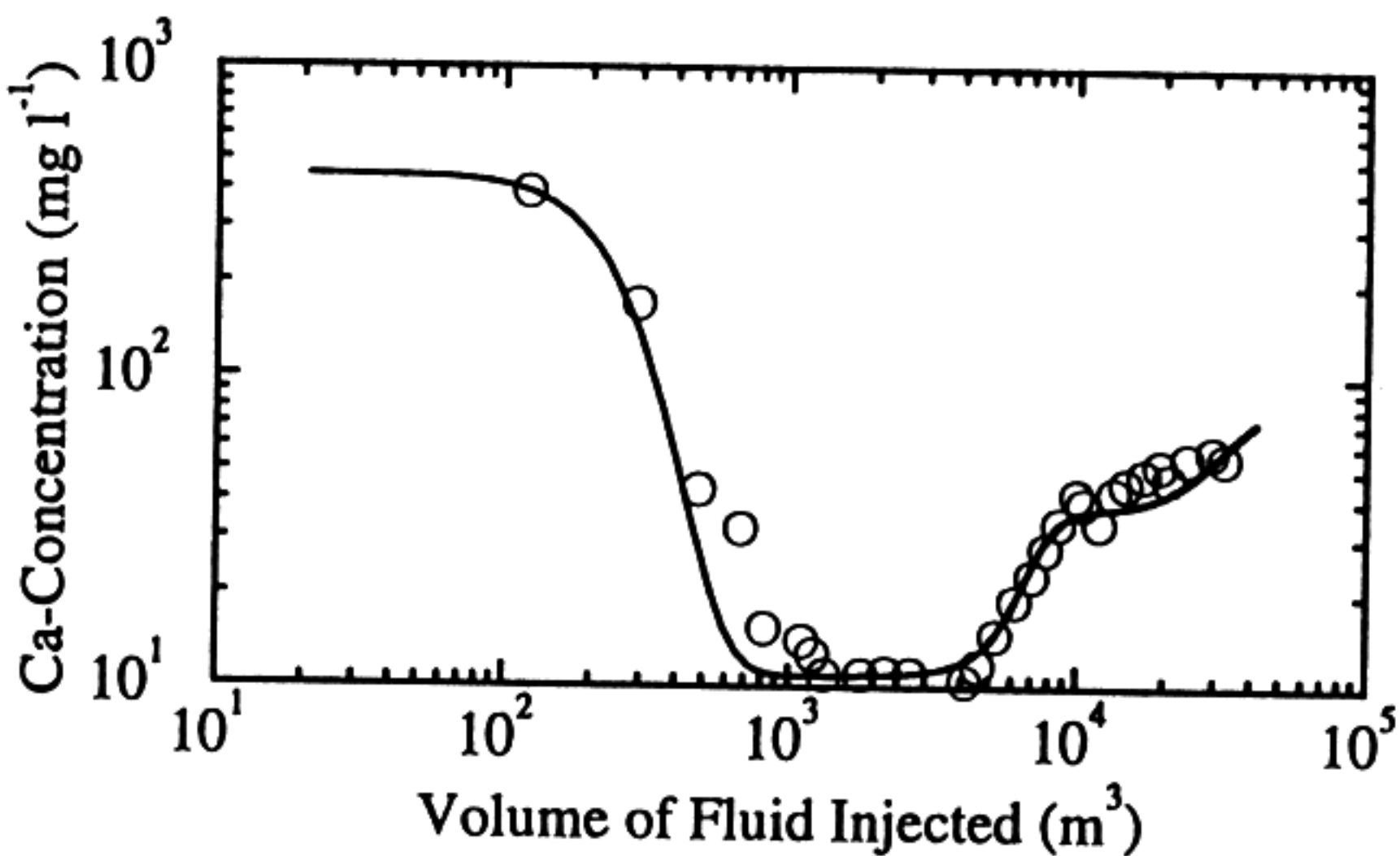FIGURE 3. Mixing cell prediction (line) and observed (circle) concentration profiles of Mg.

FIGURE 4. Mixing cell prediction (line) and observed (circle) concentration profiles of Ca.