ANALYSIS OF ONE-DIMENSIONAL MULTISPECIES TRANSPORT EXPERIMENTS IN LABORATORY SOIL COLUMNS

K. Bajracharya and D. A. Barry
Department of Environmental Engineering
Centre for Water Research
University of Western Australia
Nedlands 6009, W. A.

1. INTRODUCTION

Although single species solute transport is the norm in environmental modelling studies, in general the transport of multiple species must be considered. Even for one-dimensional transport, multiple species modelling is a computationally difficult task as results necessitate the solution of coupled, nonlinear partial differential equations. Thus, it is not surprising that considerable effort has been devoted to producing efficient and reliable codes for multispecies transport modelling [1].

The mixing cell concept is not new, and has been applied many times to predict the movement of reactive and non-reactive solutes in soil and groundwater [2-6]. For single species tracer transport, the standard mixing cell model [4] is first order accurate in the space and time discretization when a reaction is included [7]. An improved mixing cell model which maintains second-order accuracy for reactive transport was therefore developed [7]. The improved scheme is unconditionally stable, meaning that the temporal step size is unrestricted, at least with respect to stability.

Numerous researchers have presented results on the time dependence of reactions during transport [8-9]. For single species transport, the governing advection-dispersion equation is supplemented by a transformation rate equation. Bajracharya and Barry [10] demonstrated that the mixing cell approach could be applied in this case also. The main purpose of this study is to extend the single species mixing cell models of Bajracharya and Barry [7, 10] to multiple species, and to show its use in the analysis of transport problems undergoing either equilibrium or nonequilibrium reactions. The multiple species mixing cell model is assessed by comparison with a standard numerical scheme, and by comparison with experimental data. In this study, the models have been used to analyse two sets of laboratory data [9, 11].

2. GOVERNING EQUATIONS

If the only reactions taking place are adsorption or ion exchange then, for a one-dimensional homogeneous soil column, the basic equations describing the transport of reacting species considering both instantaneous and time dependent reactions can be expressed as (e.g., [12]):

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

where C_k (ML^{-3}) and S_k are the liquid and solid phase concentrations, respectively, of species k, V (LT^{-1}) is the pore water velocity, D_s (L^2T^{-1}) the dispersion coeffecient, ρ (ML^{-3}) the bulk density and θ porosity.

To solve equation 1, an additional n equations are required. The chemical reaction laws describing the ion exchange process or other surface reaction laws provide these equations. 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., [13]):

$$K_{lk} = \left(\frac{S_l^*}{C_l}\right)^{v_k}\left(\frac{C_k}{S_k^*}\right)^{v_l}, \tag{2}$$

where K_{lk} is the selectivity coefficient, v_k and v_l are constants and

$$S_k^* = \frac{S_k}{CEC}. \tag{3}$$

The additional equation is provided by the cation exchange capacity (CEC), i. e.,

$$CEC = \sum_{k=1}^{n} S_k. \tag{4}$$

The combination of equations 2, 3 and 4 result in the n multispecies exchange isotherms:

$$S_k = f_k(C_1, C_2, ..., C_n), \qquad k = 1, 2, ..., n. \tag{5a}$$

It is straightforward to extend the one site model to the two site adsorption model. For example, the instantaneously adsorbed solid phase concentration is given as the fraction (F) of the total solid phase concentration

$$S_{1k} = F\,S_k, \quad k = 1, 2, ..., n, \tag{5b}$$

whereas the adsorption pertaining to kinetic adsorption is

$$S_{2k} = (1 - F)\,S_k, \quad k = 1, 2, ..., n. \tag{5c}$$

The kinetic nonequilibrium equation is given by (e.g., [10, 14])

$$\frac{\partial S_{2k}}{\partial t} = \alpha_k[(1 - F)\,f_k(C_1, C_2, ..., C_n) - S_{2k}], \qquad k = 1, 2, ..., n. \tag{6}$$

The parameter α_k (T^{-1}) in equation 6 is the rate constant. Equations 1 - 6 constitute the two site multispecies transport model. Equation 6 states that when α_k is very large, the kth reaction approaches equilibrium and when α_k is 0, the kth reaction does not occur.

To solve equation 1, we specify initial and boundary conditions that correspond to a step function input at the boundary $z = 0$

$$C_k(z,0) = C_{kn}, \quad z > 0,$$
$$C_k(0,t) = C_{kf}, \quad t \geq 0. \tag{7}$$

where C_{kf} (ML^{-3}) and C_{kn} (ML^{-3}) are, respectively, the feed and native liquid phase concentrations of species k.

The system of nonlinear equations 1 - 6 with initial and boundary conditions 7 are here solved by the improved mixing cell model for two separate cases of equilibrium and kinetic nonequilibrium. For the equilibrium model, the constant F becomes unity and S_{1k} is equal to S_k while for fully kinetic nonequilibrium, F assumes the value zero and S_{2k} equals S_k. The nonlinear system of equations formed at each of the grid point, upon applying the method, was solved by Newton's method. The improved mixing cell model fixes the sptatial step at $2D_s/V$ and permits larger time steps to be taken than that used in the standard mixing cell model without affecting the accuracy [7].

3. ANALYSIS OF EXPERIMENTAL RESULTS USING THE IMPROVED MODEL

3.1 Snow-Plow Effect

The snow-plow effect results when a soil with a relatively low cation exchange capacity has its exchange sites on the soil particles desorbed of resident cations by an incoming solution of high solute concentration. This effect results from competition for sites between species, with more abundant ones occupying the most sites. The ions removed from the exchange sites are then forced into the interstitial solution and is pushed ahead by the incoming solution front like a snow plow. Barry et al. [11] have given a numerical analysis of this effect. Here this problem is treated using the improved equilibrium mixing cell model with labelled and unlabelled Ca^{2+} as the two species. The problem is treated as an ion exchange between labelled and unlabelled ions with a selectivity coefficient of 1. The cation exchange capacity is 0.015 meq g^{-1} and the bulk density of the soil is 1.6 g cm^{-3}. The water content was 0.37. Initially, the labelled Ca concentration in the interstitial liquid is 0.01 eq l^{-1} and the concentration of the incoming unlabelled Ca is 2 eq l^{-1}. The concentration of labelled Ca in the feed solution and the initial concentration of unlabelled Ca in the interstitial liquid are both zero. The length of the laboratory column was 5 cm.

Figure 1 shows the improved equilibrium mixing cell prediction (dashes) of the snow-plow effect for a Peclet number of 100. Note that the ordinate is the ratio of labelled Calcium to the cation exchange capacity expressed in terms of liquid phase concentration. This result is in excellent agreement with the solution of [11] (not shown in Figure 1). The figure also shows the experimental data (solid circles) of Starr and Parlange [15].

However, the prediction is far from the experimentally observed data. The equilibrium model could not fit the observed data and hence a kinetic model was tried. Better results were obtained when this model was used. A Peclet number of 272 and a rate parameter, α = 9.53 d^{-1}, described the observed data satisfactorily as shown by the solid line in Figure 1.

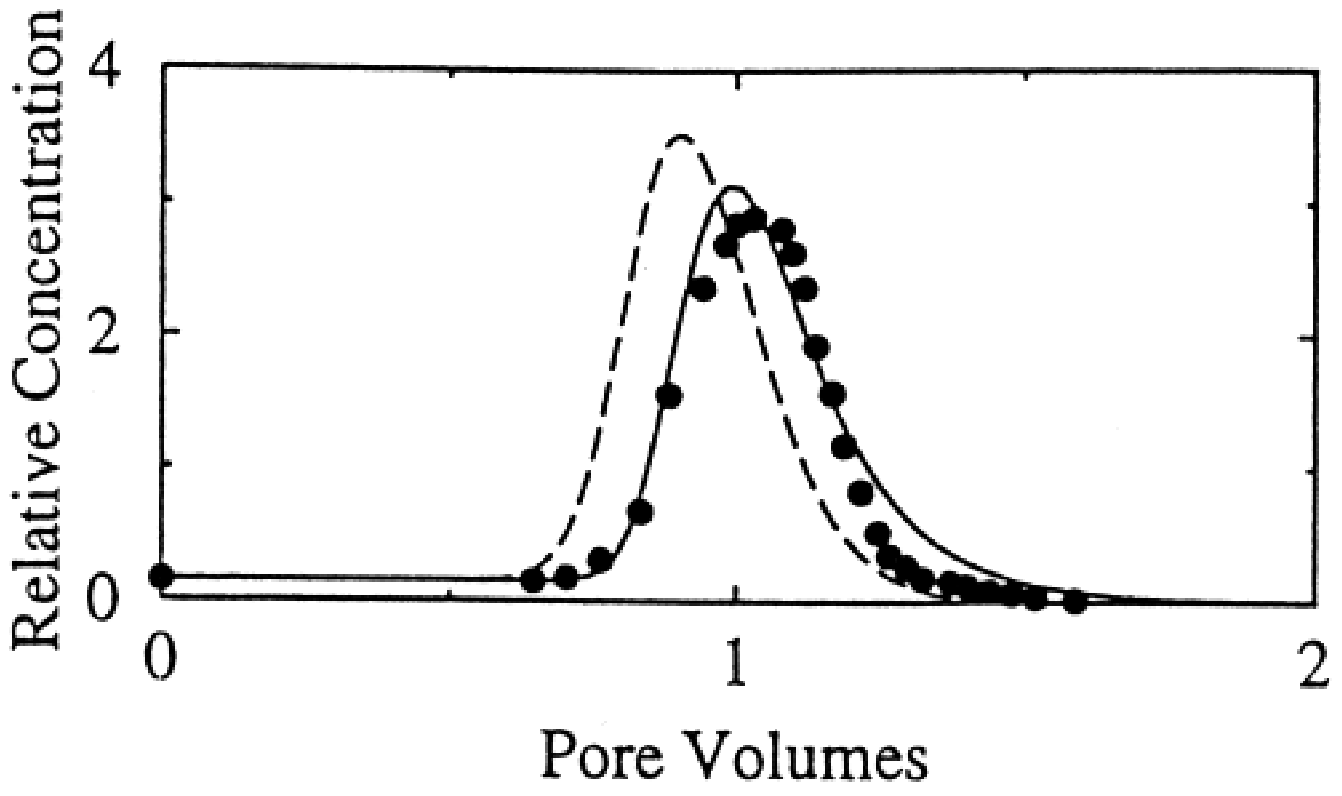

FIGURE 1
Equilibrium (dashes) and nonequilibrium (line) mixing cell predictions and observed (circle) breakthrough curve of Ca.

3.2 Binary Homovalent Ion Exchange

Schulin et al. [9] have presented a well controlled laboratory experiment on exchange reactions. Their experiment consisted of ion exchange reactions between Ca and Mg in two types of soils. The experiment was performed under conditions of variable total concentrations of Mg ions in the feed. The native solution in the soil column was initially Ca saturated. At sixteen to twenty pore volumes the Mg concentration in the feed solution was changed. The flow conditions were saturated and steady. The main chemical mechanism assumed to govern transport here is ion exchange between the two species. Here we use the improved nonequilibrium mixing cell model under varying feed total concentration to analyse the experimental breakthrough curves of Ca and Mg in the Abist loam soil. The experimental constants are shown in TABLE 1.

TABLE 1
Experimental constants of Schulin et al. [9]

Parameters	Abist Loam
Bulk Density (g l^{-1})	1286.35
CEC (meq g^{-1})	0.0543
Selectivity coefficient	0.49
Pore Water Velocity (cm d^{-1})	18.84
Dispersion Coefficient (cm^2 d^{-1})	8.48

Schulin et al. [9] using a batch evaluated selectivity coefficient found their one region transport model to result in reasonable prediction of the measured Mg-Ca breakthrough curves (BTC) for both soils. The one region model agreed with the experimental data and was particularly close in the first part of the BTC, but it overestimated the speed of Mg-Ca breakthrough and thus did not account for the second Ca snow plow peak adequately (Figure 3 of [9]). By increasing the cation exchange capacity (CEC) of the soils, Schulin et al. [9]

observed that the one region model accounted better results at the later part of the BTC but at the cost of larger deviations in the initial parts of BTC. Attempts were made to simulate the Mg-Ca BTC using a two-region model by the authors but did not result in a better prediction than the one region model.

The mixing cell solution of the equilibrium and nonequilibrium models, equations (1-6) with the parameter values reported by Schulin et al. [9] gave similar results. The authors found by conducting batch experiments that the selectivity coefficients were significantly different for the two soils but independent of the total cation concentration [9]. However, this is in contrast to the results reported by Schweich et al. [3]. Selectivity coefficients are usually assumed constant although they depend upon the composition of both phases through the activity coefficients [3]. For example, Van Ommen [4] used selectivity constants reported by Valocchi et al. [13] after correction for activity coefficients. Besides, when the total cation concentration changes, ionic strength changes, thereby changing the activities which in turn affects the selectivity coefficient (contrary to the results obtained by Schulin et al. [9]). With this reasoning, the selectivity coefficient was changed at the instant when the total Mg concentration was changed. Figure 2 shows the improved nonequilibrium model prediction of the Mg and Ca BTC for Abist loam. The initial selectivity coefficient was taken as 0.49 and, after the change in the Mg concentration, the value used was 1.5. The rate parameter and CEC were taken as 1 d^{-1} and 0.1 meq g^{-1}, respectively. It is observed that the CEC had to be also increased to get better results. The authors [9] also mention about the underestimation of CEC as obtained from batch experiments. In the present case, the increase necessary for better prediction was 84%. We note that the prediction is quite satisfactory.

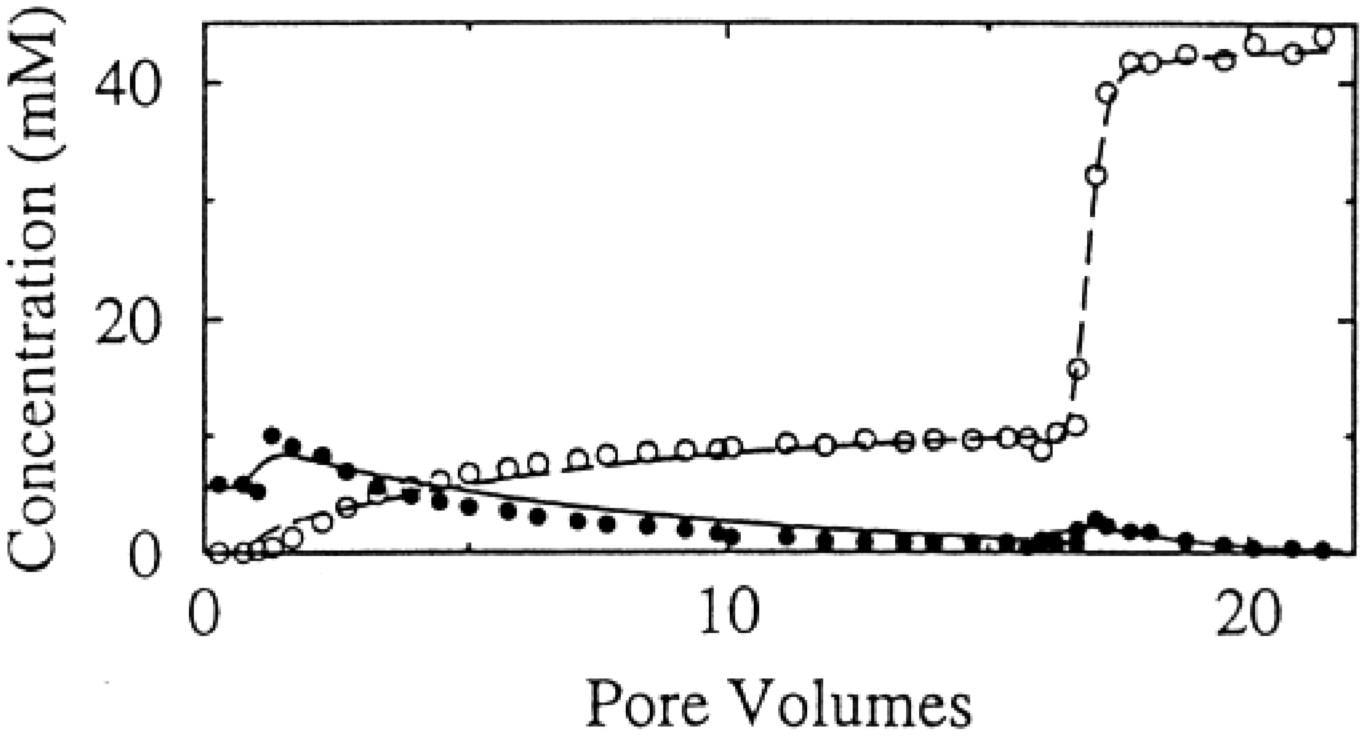

FIGURE 2
Improved nonequilibrium mixing cell predictions (dashes represent Mg and line represents Ca) and laboratory data (open circle is Mg and solid circle is Ca) for Abist loam experiments.

4. CONCLUSIONS

The mixing cell model approach has been extended to cater for the equilibrium and nonequilibrium multispecies solute transport problems. The breakthrough curves at the column exit or the concentration profiles along the column depict complex shapes characterised by plateaus and depressions. These complex profiles are dependent mainly on the native and feed solute concentrations. The snow plow is the result of certain specific native and feed solute concentrations. The present analysis of this problem using improved multispecies equilibrium mixing cell model revealed that labelled and unlabelled Ca could be treated as two species undergoing ion exchange reaction to reproduce the published results of Barry et al. [11]. However, the fully nonequilibrium model fitted the observed data better thus implying time dependent processes taking place rather than an equilibrium process.

The selectivity coefficient changes with the total cation concentration which is in accordance with the reports presented by Schweich et al. [3] and which is confirmed by the numerical analysis of the experimental data of Schulin et al. [9]. The two snow plows of Ca observed in their experiments were adequately described by changing the selectivity coefficients with the change in total cation concentration.

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References

[1] Mangold, D. C., and Tsang, C. F., A summary of subsurface hydrological and hydrochemical models. *Rev. Geophys.*, 29, 51-79, 1991.

[2] Schweich, D., and Sardin, M., Adsorption, partition, ion exchange and chemical reaction in batch reactors or in columns. *J. Hydrol.*, 50, 1-33, 1981.

[3] Schweich, D., Sardin, M., and Gaudet, J. P., Measurement of a cation exchange isotherm from elution curves obtained in a soil column: Preliminary results. *Soil Sci. Soc. Am. J.*, 47, 32-37, 1983.

[4] Van Ommen, H. C., The "mixing-cell" concept applied to transport of non-reactive and reactive components in soils and groundwater. *J. Hydrol.*, 78, 201-213, 1985.

[5] Rao, B. K., and Hathaway, D. L., Three-dimensional mixing cell solute transport model and its application. *Ground Water*, 27, 509-516, 1989.

[6] Dudley, L. M., Mclean, J. E., Furst, T. H., and Jurinak, J. J., Sorption of cadmium and copper from an acid mine waste extract by two calcareous soils: Column studies. *Soil Sci.*, 151, 121-135, 1991.

[7] Bajracharya, K., and Barry, D. A., Mixing cell models for nonlinear equilibrium single species adsorption and transport. *J. Contam. Hydrol.*, 12, 227-243, 1993.

[8] Rubin, J., Transport of reacting solutes in porous media: Relation between mathematical nature of problem formulation and chemical nature of reactions. *Water Resour. Res.*, 19, 1231-1252, 1983.

[9] Schulin, R., Parpritz, A., Fluhler, H., and Selim, H. M., Calcium and Magnesium transport in aggregated soils at variable ionic strength. *Geoderma*, 44, 129-141, 1989.

[10] Bajracharya, K., and Barry, D. A., Mixing cell models for nonlinear nonequilibrium single species adsorption and transport. *Water Resour. Res.*, 29, 1405-1413, 1993.

[11] Barry, D. A., Starr, J. L., Parlange, J.-Y., and Braddock, R. D., Numerical analysis of the snow-plow effect. *Soil Sci. Soc. Am. J.*, 47, 862-868, 1983.

[12] Barry, D. A., "Modelling contaminant transport in the subsurface: Theory and computer programs" in *Modelling Chemical Transport in Soil: Natural and Applied Contaminants*, eds. Ghadiri, H. and Rose, C. W., pp. 105-144, Lewis Publishers, Chelesea, Mich., 1992.

[13] Valocchi, A. J., Street, R. L., and Roberts, P. V., Transport of ion-exchanging solutes in groundwater: Chromatographic theory and field simulation. *Water Resour. Res.*, 17, 1517 - 1527, 1981.

[14] van Genuchten, M. Th., and Wierenga, P. J., Simulation of one dimensional solute transfer in porous media. New Mexico Ag. Exp. Sta. Bull. 628, Las Cruces, NM, 1974.

[15] Starr, J. L., and Parlange, J. -Y., Dispersion in soil columns: The snow-plow effect. *Soil Sci. Soc. Am. J.*, 43, 448-450, 1979.