A Tool for Evaluating a Need for Variable Selectivities in Cation Transport in Soil

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The empirical Rothmund-Kornfeld equation was used to describe a collection of cation exchange isotherms for K and Ca in Brucedale soil over a range of total solution concentrations (C_T). A comparison of variable binary exchange selectivity coefficients (K_{KCa}) which vary with C_T and solution phase ion concentrations (C_K, C_{Ca}) with constant K_{KCa} values was thus possible. Percent differences between sorbed equilibrium concentrations calculated using variable and constant K_{KCa} over a range of C_T and C_K were arranged into a contour map. Zones of potentially observable difference were limited, implying that simulations of cation transport using variable and constant K_{KCa} values would be essentially identical. The predicted effect was examined using a numerical model for cation transport. The model successfully described observed spatial distributions for cation concentrations following constant-flux infiltration of electrolyte solution into soil columns. Simulations using variable K_{KCa} values provided only a slight improvement over simulations using constant K_{KCa} values, thus validating the use of the contour map as a convenient method to evaluate the need to use variable selectivities in simulations of cation transport.

INTRODUCTION

Total solution concentration (C_T) is well known to impact heterovalent cation exchange in soils, and binary exchange isotherms are typically performed with constant C_T imposed. In general, aluminosilicate clay mineral ion exchangers prefer counterions of higher valence, and this preference increases with dilution (decreasing C_T) of the solution [*Helfferich*, 1962]. For example, during binary exchange involving monovalent and divalent species, dilution tends to enhance the adsorption of the divalent but inhibit adsorption of monovalent species. Thus variable C_T implies the need for variable K_{KCa} in ion transport models.

Recently, *Bond and Phillips* [1990c] asserted that spatial and temporal changes in C_T during transient, unsaturated water flow in soils may have minimal impact upon the transport of heterovalent cations in the solution phase and resulting distributions of cations in the soil exchange phase. Variable C_T may occur during a simple case of constant-flux infiltration of aqueous influent with C_{To} into water-unsaturated soil where the initial solution $C_{Tn} \neq C_{To}$. For that case, the advancing zone of cation exchange is retarded with respect to liquid flow and occurs well behind the advancing front for C_T. Displacement of solution initially present in the soil results in the wetting front's moving well ahead of the moving C_T front. The implication is that as liquid flow proceeds and chromatographic separation of cation species occurs, exchange is predominantly controlled by the influent C_{To}.

A multi-ion transport model with assumptions of instantaneous exchange, constant exchange selectivity coefficients K_{ij} for each binary pair of competing ion species i and j, constant cation exchange capacity S_T, variable total solution

concentration C_T, and steady water flow was presented by *Rubin and James* [1973] and *Valocchi et al.* [1981]. That model was later modified by *Mansell et al.* [1988] in order to permit K_{ij} to vary with ion concentrations for species i (C_i) in the soil solution phase for conditions of invariant C_T. More recently, Rothmund-Kornfeld-type formulations for exchange isotherms were incorporated into that transport model to allow K_{ij} selectivity values to vary as functions of both C_i and C_T parameters [*Mansell et al.*, 1993].

The objective for this work was to evaluate the influence of C_T upon cation exchange and transport during water flow in soil. A model presented recently [*Mansell et al.*, 1993] for describing the simultaneous transport of multiple species of cations during conditions of transient solution normality (C_T) and transient liquid flow in unsaturated soil was used in the evaluation.

MATHEMATICAL MODEL

In the model presented by *Mansell et al.* [1993] the Gaines-Thomas binary exchange selectivity coefficient [*Valocchi et al.*, 1981] is given as

$$K_{ij} = \frac{[\gamma_j]^{r_i}}{[\gamma_i]^{r_j}} \left[\frac{S_i^*}{C_i}\right]^{r_j} \left[\frac{S_j^*}{C_j}\right]^{-r_i} \tag{1}$$

where S_i^* and S_j^* represent equivalent fractions of ions i and j in the exchange phase and γ_i and γ_j are the activity coefficients for ions i and j, respectively, in the solution phase. *Valocchi et al.* [1981] stated that inclusion of solution phase activity coefficients is only necessary for the description and prediction of cation exchange if ionic strengths corresponding to experimental isotherms differ from those used in transport experiments. Since exchange isotherms to be reported here revealed little dependence upon ionic strength, γ_i and γ_j in (1) were set to unity for the simulations. Thus setting $\gamma_i = \gamma_j = 1$, (1) can be written as
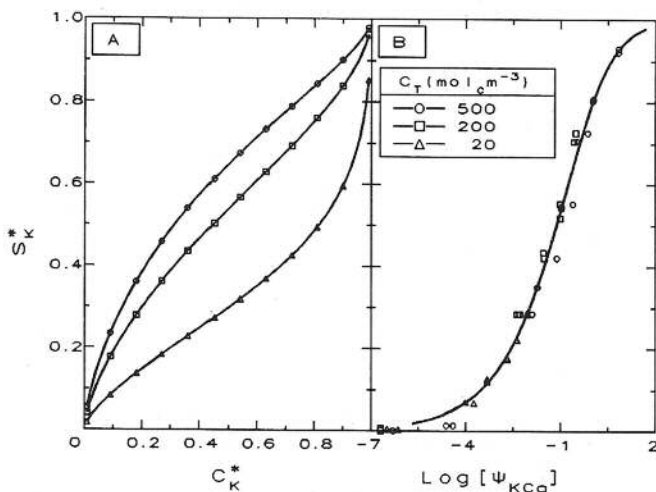
Fig. 1. (a) Rothmund-Kornfeld exchange isotherms (S^* versus C^*) for K-Ca reaction in Brucedale soil for three values of C_{To} (20, 200, and 500 mol_c m^{-3}). (b) A single Rothmund-Kornfeld plot of S^*_K versus C^2_K/C_{Ca} for K-Ca reaction over a range of C_{To} for Brucedale soil. Data are indicated by open circles, triangles, and squares.

$$K_{ij} = \tau_{ij} \psi_{ij}^{-1} \qquad (2)$$

where

$$\tau_{ij} = \frac{(S^*_i)^{r_j}}{(S^*_j)^{r_i}} \qquad (3)$$

$$\psi_{ij} = [C_T^{r_i - r_j}] \left[\frac{(C^*_i)^{r_j}}{(C^*_j)^{r_i}} \right] \qquad (4)$$

The parameters C^*_i and C^*_j represent equivalent fractions of ion species i and j in the solution phase. In (4), ψ_{ij} is a function of C^*_i for homovalent and heterovalent exchange but varies with C_T only for heterovalent exchange.

The Rothmund-Kornfeld-type exchange isotherm [Bond and Phillips, 1990b; Mansell et al., 1993],

$$\tau_{ij} = k_{ij} \psi_{ij}^{n_{ij}} \qquad (5)$$

can be used to provide a convenient empirical mathematical expression for describing experimental cation exchange isotherms, where the empirical constants k_{ij} and n_{ij} can be evaluated using least squares fitting techniques. Substitution of (5) into (3) provides a practical mathematical expression for K_{ij} that varies with C^*_i and C_T:

$$K_{ij}(C^*_i, C_T) = k_{ij} \psi_{ij}^{n_{ij}-1} \qquad (6)$$

Thus the Rothmund-Kornfeld parameter n_{ij} allows the selectivity coefficient K_{ij} to vary with local composition of the soil solution phase. When $n_{ij} = 1$ and/or homovalent exchange occurs, (6) predicts that K_{ij} is a constant (equal to k_{ij}) with respect to C^*_i for a given C_T as used by Valocchi et al. [1981]. For $n_{ij} < 1$ and occurrence of heterovalent exchange, (6) predicts K_{ij} to vary nonlinearly with both C^*_i and C_T.

RESULTS AND DISCUSSION

Exchange isotherm data for K-Ca pairs [Bond and Phillips, 1990a] for three C_T values (20, 200, and 500 mol_c m^{-3}) are presented in Figure 1a for Brucedale soil (mol_c indicates

TABLE 1. Physical Parameters for Constant-Flux Infiltration Experiments With Soil Columns

Parameter	Magnitude
Soil bulk density (ρ), Mg m^{-3}	1.0
Initial water content (θ_n), m^3 m^{-3}	0.16
Initial solution normality (C_{Tn}), mol_c m^{-3}	135
Dispersivity (α), m	0.001
Diffusion coefficient (β_0), m^2 s^{-1}	1.1×10^{-9}
Saturated water content (θ_s), m^3 m^{-3}	0.53
Applied water flux (v_0), m s^{-1}	1.447×10^{-6}
Infiltration duration (t_f), s	23,150
Scaled wetting front penetration ($X_f = v_0 X_f$), m^2 s^{-1}	2.17×10^{-7}
Scaled termination time ($T_f = v_0^2 t_f$), m^2 s^{-1}	4.85×10^{-8}
Node spacing used during simulations, m	1.5×10^{-3}
Maximum time step used during simulations, s	10

moles of charge). Least squares fitting of the Rothmund-Kornfeld equation to these data provided optimum values of 0.695 and 3.108×10^{-3} m^3 mol_c^{-1} for k_{KCa} and n_{KCa}, respectively, for K-Ca exchange reaction over the entire experimental range for C_T (Figure 1b). The n_{KCa} value of 0.695 for K-Ca indicates nonlinear exchange so that K_{KCa} values vary with both C_K and C_T. The presence of 2 : 1 layer clay minerals in this soil resulted in a relatively high preference of exchange sites for K over other monovalent ions as well as a moderate preference over divalent Ca ions [Bond and Phillips, 1990a]. This soil was strongly aggregated (aggregate diameter < 0.35 mm) and structurally stable. The total clay content was in excess of 60% and $S_T = 222$ mol_c Mg^{-1} (Table 1). The Illitic nature of the clay and the initial presence of 2.3% of K in the exchange phase indicate that exchange sites in this soil have a preference for K over Ca divalent ions. The isotherms indicate that the relative preference of soil exchange sites for K over Ca depends upon the solution C_T (Figure 1a). Although specific adsorption of K at interlayers has been suggested for this soil, time dependency due to diffusion-limited ion exchange was not observed during constant-flux infiltration in the soil columns [Bond and Phillips, 1990b].

The Rothmund-Kornfeld equation (5) is empirical in basis, but it provides a valuable mathematical means to fit binary exchange isotherm data for a range of C_T values in order to give a single functional description (Figure 1b) of selectivity coefficients K_{KCa} as given by (6). Plots of calculated K_{KCa} (equation (6)) over the range $0.01 \leq C^*_K \leq 0.99$ reveal the highly nonlinear relationship between K_{KCa} and C^*_K for K-Ca exchange for the Brucedale soil (Figure 2). Exchange selectivity coefficients for K-Ca exchange for either 20 or 200 mol_c m^{-3} have maximal and minimal magnitudes corresponding to $C^*_K < 0.1$ and $C^*_K > 0.9$, respectively, with a smooth transition in between. However, for any given C^*_K, values of K_{KCa} were largest for the more dilute ($C_{To} = 20$ mol_c m^{-3}) solution. A tenfold increase in C_T from 20 to 200 mol_c m^{-3} resulted in a decrease in K_{KCa} which was considerably less than tenfold. The geometric exchange selectivity coefficients $[K_{KCa}]_g$ were decreased approximately twofold from 13.801×10^{-3} to 6.839×10^{-3} m^3 mol$_c^{-1}$ (Table 2) for the tenfold increase in influent solution normality C_{To} from 20 to 200 mol_c m^{-3}. Thus concentrating the aqueous solution by increasing C_T tended to decrease the relative pref-
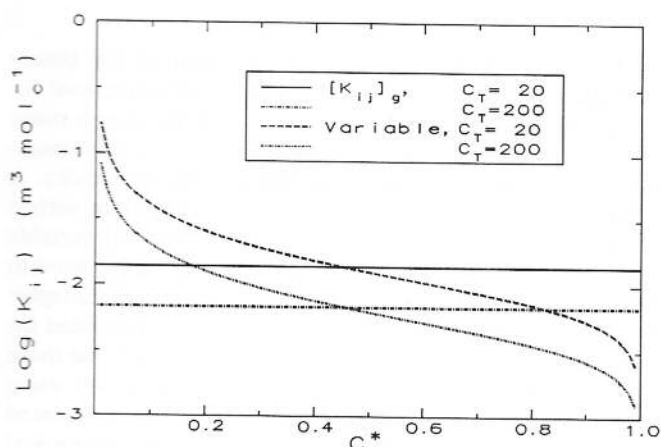
Fig. 2. Calculated constant and variable exchange selectivity coefficients K_{KCa} as functions of C_K^* with total solution concentrations of 20 and 200 mol_c m^{-3} for K-Ca exchange.

Fig. 3. Contours of percentage discrepancy between sorbed phase concentrations of K calculated with constant (S_C) and variable K_{KCa} values (S_V) relative to the S_T.

erence of exchange sites for K over Ca in the Brucedale soil (Figure 2).

Bond and Phillips [1990a] reported constant-flux infiltration of electrolyte solutions into horizontal columns of Ca-saturated Brucedale soil under conditions of transient soil water content $\theta(x, t)$, water flow velocity $q(x, t)$, $C_K(x, t)$, $C_{Ca}(x, t)$, and $C_T(x, t)$, where x and t are distance and time, respectively. Salt solutions were applied using three liquid flux ν_0 values (0.723×10^{-6}, 0.964×10^{-6}, and 1.447×10^{-6} m s^{-1}) for corresponding termination times (t_f) of 92,800, 52,200, and 23,150 s, respectively [*Bond and Phillips*, 1990a]. The initial soil water content (θ_n) was 0.16 m^3 m^{-3}, and the normality (C_{Tn}) of the solution initially present in the soil was 135 mol_c m^{-3}. Total solution concentrations for invading salt solutions C_{To} were 20, 100, and 200 mol_c m^{-3}. Results from only 200 mol_c m^{-3} were simulated and reported here. Wetting front penetration distances (x_f) were 0.30, 0.22, and 0.15 m, corresponding to liquid fluxes of 0.723×10^{-6}, 0.964×10^{-6}, and 1.447×10^{-6} m s^{-1}. Each flux and termination time pair was chosen to provide a common scaled termination time $T_f = 4.85 \times 10^{-8}$ m^2 s^{-1} and a common scaled wetting penetration distance $X_f = 2.17 \times 10^{-6}$ m^2 s^{-1}, where $T = \nu_0^2 t$ and $X = \nu_0 x$ [*White*, 1979]. The highest value for ν_0 was used in model simulations for cation transport (Table 1).

Contours of percentage discrepancy between sorbed phase concentrations of K calculated with constant (S_c) and with variable K_{KCa} values (S_v) relative to the soil cation exchange capacity S_T are reported in Figure 3 over the

ranges $0.01 < C_K^* < 0.99$ and $0.001 < C_T < 1.0$. This discrepancy was calculated as $D = 100[S_c - S_v]/S_T$ where sorbed phase concentrations were determined using the following solution for the binary quadratic equation;

$$S = [-b + (b^2 - 4ac)^{1/2}]/2a \qquad (7)$$

where

$$a = C_{Ca}/S_T K_{KCa} C_K^2 \qquad b = 1 \qquad c = -S_T$$

and the geometric mean $[K_{KCa}]_g$ or (6) was used, respectively, for the selectivity term K_{KCa} in obtaining S_C or S_V.

The contour map of the discrepancy D between sorbed K concentrations calculated with constant and variable K_{KCa} relative to the S_T value revealed zones where $D > 10\%$ and where $D < -10\%$. The zones of maximum discrepancy correspond to the areas of maximum difference between the geometric mean selectivity and appropriate variable selectivities (Figure 2). In general, however, the discrepancy was relatively small for K-Ca exchange for the Brucedale soil under these conditions.

The technique of generating a contour map to determine the likelihood of significant differences between constant and variable selectivities can be used as a guide in deciding whether the increased complexity of using variable selectivities in a cation transport model for a given soil is justified. That decision is, of course, influenced by the maximum potential discrepancy along the projected path across the contour map taken in light of expected experimental error. In this particular case of transport of K and Ca in Brucedale soil, it is unlikely that there would be an appreciable difference in predictions of cation transport based on constant or variable selectivities.

A simulation of the transient water flow for the highest infiltration flux provided a reasonable description of spatial distributions of volumetric water content $\theta(X, T_f)$ observed after termination of horizontal infiltration for all three imposed liquid fluxes [*Mansell et al.*, 1993]. Due to observed

TABLE 2. Selectivity Coefficients and Fitted Parameters for Column Experiments

C_{To}, $mol_c m^{-3}$	$[K_{KCa}]_g$, 10^{-3} m^3 mol_c^{-1}	Regression Parameters	
		k_{KCa}, 10^{-3} m^3 mol_c^{-1}	n_{KCa}
20	13.801	3.1079	0.695
200	6.8394	3.1079	0.695

The influent solution is KCl (K$^+$ → Ca^{2+}). Values of k_{KCa} and n_{KCa} parameters are obtained by least squares fitting of the Rothmond-Kornfeld equation to cation exchange isotherms for the K-Ca reaction. Geometric means for binary exchange selectivity coefficients $[K_{KCa}]_g$ on respective binary isotherms are also presented.
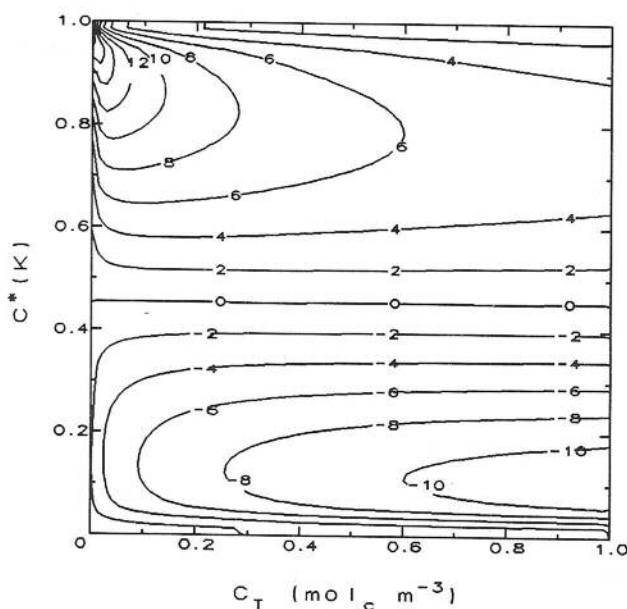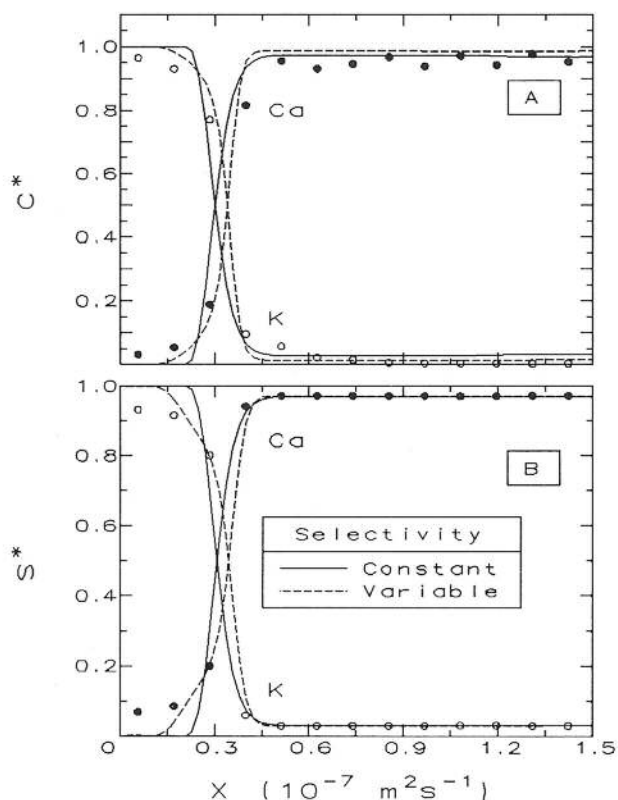
Fig. 4. Experimental (discrete points) and simulated distributions of C_K^* and S_K^* for K and Ca with scaled distance X after infiltration with 200 mol_c m^{-3} normality KCl. Solid and dashed lines were simulated with the general model using variable and fixed K_{KCa} values, respectively.

CONCLUSIONS

The empirical Rothmund-Kornfeld equation for binary exchange isotherms was shown to be an effective tool for describing changes in ion exchange selectivity over a range of total solution concentrations and relative ion concentrations and is thus useful for modeling variable selectivity. A contour map of differences between the equilibrium sorbed phase concentrations calculated with constant and variable selectivities is suggested as a tool for evaluating the need to use variable selectivities when simulating cation transport for a given isotherm. Such a contour map was generated for K and Ca exchange in Brucedale soil and indicated that there would be relatively little difference in simulations using constant or variable selectivities. This prediction was tested by using variable and constant selectivities in a numerical mathematical model to describe the simultaneous transport of multiple species of cations during conditions of transient solution C_T and transient liquid flow in unsaturated soil constant-flux infiltration. Under both selectivity regimes, the model was able to closely simulate data from constant-flux experiments where single-salt (KCl) input solutions with one normality (C_{To}) were applied to Ca-saturated soil with initial water content (θ_n) and a different soil solution normality (C_{Tn}). The results of the simulation using variable selectivities appeared to be slightly superior to the results of the simulation using constant selectivities, but the differences were of the same order of magnitude as the experimental error, thus supporting the predictive capability of the contour map.

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anion exclusion [*Bond and Phillips*, 1990*a*], tritiated water tracer did not behave as a conservative solute, but the model described the terminal distributions of ^3H_2O concentration in the soil solution. Along the front for tritiated water, simulated and experimental results varied by less than 0.60%.

A comparison of simulated and experimental results for spatial distributions of ion concentrations in the solution phase $C_K^*(X, T_f)$ and $C_{Ca}^*(X, T_f)$ and ion concentrations in the exchange phase $S_K^*(X, T_f)$ and $S_{Ca}^*(X, T_f)$ corresponding to the termination time for the experiment using $v_0 = 1.447 \times 10^{-6}$ m s^{-1} is shown in Figure 4. Constant and variable K_{KCa} values were both effective in describing cation transport. The sharp C_K^* profiles clearly reflect the greater selectivity of K over Ca for $C_{To} = 200$ mol_c m^{-3} in this soil. Simulations based upon assumptions of constant (geometric mean $[K_{KCa}]_g$) and variable K_{KCa} in the transport simulations gave essentially minor differences when compared to experimental results. However, simulations based upon constant selectivities tended to give more abrupt changes in simulated cation distributions as compared to simulations based upon variable selectivities or as compared to the observed values. The experimental error in the observed data was estimated to be no more than 7% by noting the difference between the expected sorbed concentrations at $X \simeq 0$ (1.0 for K) and the actual values (0.93) (Figure 4). Since this value is approximately equal to the potentially observable discrepancy between constant and variable selectivities, neither selectivity regime is clearly superior.