



Soil and Water Science

Research Brief

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Transport of Multiple Cations During Water Infiltration into Unsaturated Soil

R. S. Mansell, W. J. Bond, and S. A. Bloom

During rain or irrigation following application of fertilizer or lime to soil, water infiltration into the soil tends to initiate convective-dispersive transport of ionic solutes such as Ca^{2+} through the soil profile. Physiochemical reactions such as cation exchange tend to retard solute transport for an invading cation relative to rates of water movement in soil. Cation exchange for metallic inorganic ions such as Ca^{2+} is generally assumed to occur instantaneously and reversibly in soil-water systems.

Cation transport in soils typically involves competitive exchange among multiple species (e.g., Ca^{2+} , Na^+ , and K^+) present in the invading solution, initially resident on exchange sites (mineral and organic), initially in the soil solution, and initially as salts in very dry soil. Exchange selectivity coefficients K_{ij} for each binary combination of cation species i and j are commonly used to describe competitive exchange among multiple ion species in soils.

Soil exchange sites generally prefer counter ions of highest valence, and this preference increases with dilution of the solution. For example, during binary heterovalent exchange involving monovalent

and divalent cation species, an increase in total solution concentration or normality (C_T) in the soil solution tends to enhance adsorption of monovalent species. Thus, variable C_T implies the need for variable binary ion exchange coefficients in cation transport models.

Numerical models for both water and solute were used to describe the transport of Ca^{2+} , Na^+ , and K^+ cation species during constant-flux infiltration of aqueous electrolyte (NaCl-KCl) solutions in columns of water-unsaturated Brucedale soil initially saturated with Ca^{2+} cations. Exchange sites in this soil with Illitic clay have a strong preference for K^+ over Na^+ monovalent ions as well as a preference for K^+ over divalent Ca^{2+} . The Brucedale soil was strongly aggregated and structurally stable. The total clay content was in excess of 60 % and the CEC or S_T was $228 \text{ mol}_c \text{ Mg}^{-1}$. Constant and variable exchange selectivity coefficients were used in simulations (Fig. A).

Invading NaCl-KCl salt solutions ($C_T = 200 \text{ mol}_c \text{ m}^{-3}$ with equal charge concentrations of Na^+ and K^+) were applied using a liquid flux L_o value of $1.447 \times 10^{-6} \text{ m s}^{-1}$ resulting in a termination time (t_f) of 20,800 s and a wetting-front penetration distance (x_f) of 15 cm. Initially, $Z = 0.16$ and $C_T = 75 \text{ mol}_c \text{ m}^{-3}$ in the soil solution. At saturation Z_{sat} is 0.53.

Terminal distributions of Z/Z_{sat} (Fig. B), solution-phase (C_i^*) and exchange-phase

(S_i^*) cation concentrations (Fig. C) were scaled by plotting on a reduced distance coordinate ($X_f = L_o x_f$ where L_o is the water flux at $x = 0$). Simulations successfully described experimental data.

Use of variable selectivities in simulations provided only a small improvement in terminal ion concentrations. This is in agreement with recent findings that binary cation transport during constant-flux infiltration in unsaturated soil is relatively insensitive to transient C_T since maximum cation exchange tends to occur in a mobile exchange zone well behind the moving C_T and volumetric water content (2) fronts. As infiltration proceeds the mobile ion exchange and wetting zones in the soil undergo progressive separation with time.

Authors:

R. S. Mansell and S. A. Bloom; 2169 McCarty Hall;
 PO Box 110290; Soil and Water Science
 Department; University of Florida;
 Gainesville, FL 32611-0290; Phone: (352)
 392-1956
 W. J. Bond; CSIRO; Canberra, ACT 2601, Australia

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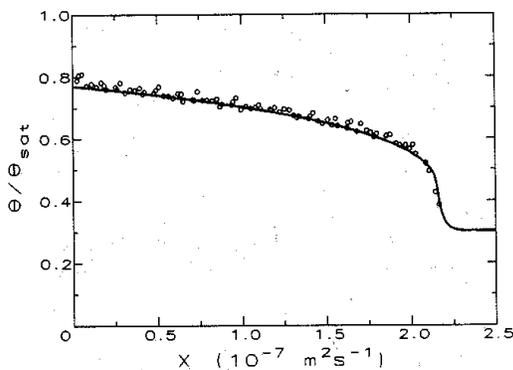


Fig. A. Terminal water content distribution with scaled distance X (Fig. 3 in Mansell et al. 1993)

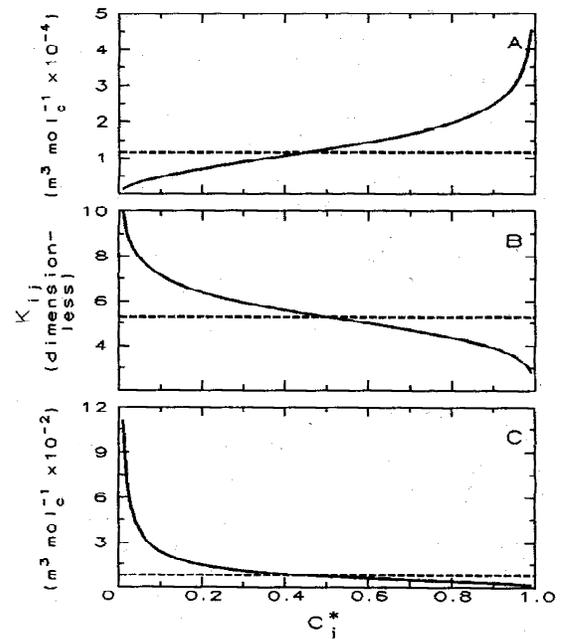


Fig. B. Selectivity coefficients for A.) Na-Ca, B.) K-Na, and C.) K-Ca (Mansell et al. 1993)

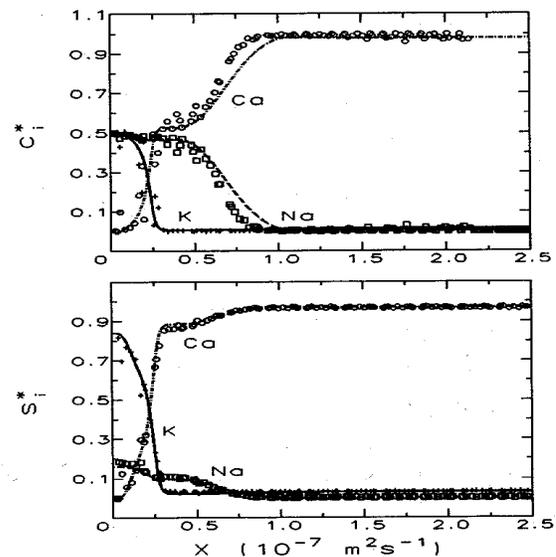


Fig. C. Observed (points) and simulated distributions of cation equivalent fractions in solution (C^*) and in exchange phases (S^*) (Mansell et al. 1993)