UNSATURATED TRANSPORT OF INORGANIC CATIONS IN UNDISTURBED SOIL COLUMNS

P.M. Jardine and G.K. Jacobs
Environmental Sciences Division
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6038

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ABSTRACT

The unsaturated transport of Sr, Co, and Ca were studied in undisturbed soil columns (14 X 40 cm) of saprolitic shale to evaluate the significance of time-dependent mass transfer and multispecies competitive exchange during transport. Observed breakthrough curves (BTCs) for Sr and Co were delayed relative to nonreactive Br BTC indicating that the former tracers were adsorbed by the soil. Effluent concentrations of Sr and Co were modeled with the classical convective-dispersive (CD) equation and nonequilibrium mass transfer considerations did not appear necessary. Cation exchange equilibria relationships obtained from both shake batch and miscible displacement methods adequately described the thermodynamic processes which were prevalent during transport. These results suggest that the preferential transport of a reactive tracer is negligible for the realistic unsaturated conditions used in this study, and that the massive saprolite within the soil is a chemically active constituent during transport of reactive solutes. The implications of these findings for modeling in-situ subsurface contaminant transport are discussed.

INTRODUCTION

Prolonged disposal of organic and inorganic waste in shallow burial sites of eastern Tennessee, has prompted detailed investigations of contaminant transport processes in upper subsurface media. The radionuclides ^{90}Sr and ^{60}Co are of significant concern because of (1) the large inventories present in existing waste sites, (2) their relatively long half-lives (~29 and ~5 years, respectively), (3) the large health risks associated with each isotope, and (4) their high mobility at many waste sites. Transport processes present at these sites are spatially complex due to preferential flow in fractured media and the presence of massive saprolite with variable size and permeability. Field experiments have indicated that preferential flow along macro- and mesopores may potentially constitute 73% of the flux during storm events (Watson and Luxmoore, 1986). Solute mobility under these conditions is largely controlled by the physical aspects of the soil (Jardine et al. 1988). Frequently, rainfall events

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in eastern Tennessee are not of sufficient size or intensity to cause flow in macropores and solute transport processes are confined to meso- and micropore domains. Under these unsaturated conditions, both chemical and hydrologic factors control the subsurface transport of solutes. Quantifying in-situ contaminant transport will thus require knowledge of fundamental hydrologic and chemical processes. The purpose of this research was to investigate the thermodynamic and kinetic processes controlling the transport of Sr, Co, and Ca in unsaturated, heterogeneous soils.

MATERIALS AND METHODS

Site Description and Sample Preparation

Large, undisturbed soil columns were isolated from a proposed waste area on the Oak Ridge Reservation in eastern Tennessee. The site has a very shallow soil profile (0.5-2m) and is underlain by saprolite present as weathered limey shale. For discussion purposes, the saprolitic material will be included in the term soil. The soils are characterized by pH and CEC values of 4.5 to 6 and 10 to 15 cmol+/kg, respectively. The clay fraction is composed primarily of illite with lesser quantities of 2:1 interstratified material and vermiculite. A large quantity of amorphous Fe-oxides are present in these soils as coatings on clay minerals (Jardine et al., 1989).

Undisturbed soil columns (14 X 40cm) used in displacement experiments were isolated from excavated pits within the B horizon and underlying saprolite. The columns were slowly shaped into their final form by careful removal of soil and clipping of roots. Paraffin wax was painted on the outer layer of soil to help maintain the integrity of the soil structure as the column was prepared. The isolated column was finally cast in a layer of wax surrounded by two coats of a rigid epoxy resin. The columns were transported to the laboratory where 3 air vents were fitted in the column sides and 2 fritted glass endplates (b.p. ~20 cm) were sealed in good contact with the soil column ends (Fig. 1).

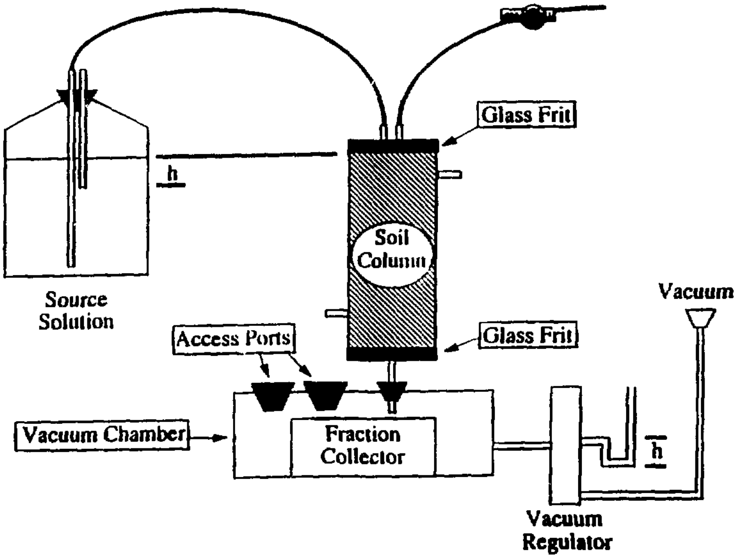

Figure 1. Schematic diagram of the unsaturated flow apparatus illustrating the constant tension design.

Miscible Displacement Experiments

Initially, soil columns were slowly saturated with $CaCl_2$ (0.05 M) from the bottom. The columns were then allowed to drain under a desired tension, with the inlet tension maintained with a mariotte device and the outlet tension maintained with a constant vacuum source (Fig. 1). A unit hydraulic gradient was established within the column by placing the inlet and outlet under the same tension. For most displacement experiments, a tension of 10 cm was selected because it allowed macropores (diameter >1 mm) in the soil columns to remain empty. This condition closely mimics the natural flow characteristics of the soil where most unsaturated flow occurs through mesopores (0.3 mm < diameter < 1 mm) and micropores (<0.3 mm).

When a steady state flux was established, nonreactive Br and reactive Sr and Co tracers were independently introduced into the columns to quantify the dispersion and nonequilibrium mass-transfer features of the soil. Both continuous and pulse additions of tracer were studied with the carrier solution of the latter being $CaCl_2$. Effluent was monitored for pH, for Co, Sr, and Ca using atomic absorption spectrophotometry (AA) and for Br using an ion specific electrode.

Cation Exchange Equilibria

Thermodynamic processes controlling the transport of Sr, Co, and Ca in soil were evaluated on bulk soil samples (moist sieved through a 2mm screen) obtained in the same vicinity as the undisturbed columns. Because the subsurface media consisted of massive fractured saprolite which is >2mm and may be partially excluded from transport processes, two types of bulk samples were obtained; (1) subsamples that were moist sieved (<2 mm) in an unaltered state (i.e. saprolite excluded) and (2) subsamples that were moist sieved after the massive saprolite had been physically disaggregated (i.e. saprolite included).

Cation exchange equilibria relationships for Sr-Co-Ca binary systems were evaluated at constant ionic strength, pH, and temperature using miscible displacement and shake batch methods. The former method involved leaching subsamples of the soil for ~7 d with various binary cation systems using $CaCl_2$, $SrCl_2$, and $CoCl_2$. Soils were equilibrated with eleven solutions of varying molar ratio for each of the binary systems which were maintained at a constant ionic strength ($I=0.003$), pH=5.6, and temperature (298K). Once equilibrium was established, the samples were washed with several small aliquots of deionized water to remove entrained salts. The adsorbed solid phase cations were then extracted with known volumes of 0.1 mol/L $LaCl_3$ with Sr, Co, and Ca analyzed by AA.

Cation exchange equilibria relationships were also evaluated using shake batch methods. Known quantities of air dried, Ca-saturated soil (0.4 to 0.8 g) were equilibrated with 30 ml of each of the eleven binary cation solutions discussed above. After 7 d equilibration, the samples were centrifuged and the supernatant analyzed for pH, and Sr and Co using AA.

THEORETICAL

Thermodynamic equilibrium constants for each binary cation exchange system were determined from the isotherms using the Vanselow equation as described by Argersinger et al. (1952) and Jardine and Sparks (1984). The equilibrium adsorption isotherms were used as model input functions for predicting contaminant transport through the undisturbed columns.

The unsaturated breakthrough of Sr and Co through the undisturbed soil columns were modeled with various equilibrium and nonequilibrium transport models based on the convective-dispersive equation (Parker and van Genuchten, 1984; Parker and Jardine, 1986). Since adsorption isotherms obtained in this study were slightly nonlinear to linear, we utilized the transport model of Parker and van Genuchten (1984) which assumes linear adsorption. A more rigorous treatment of nonlinear adsorption during transport will be dealt with in the future using the model of Parker and Jardine (1986) and will not be discussed here. In this study, model parameters used to predict single species cation transport were independently calculated, except where applicable, the first-order mass-transfer coefficient (α) and the fraction of equilibrium vs. kinetic sites (F). Some of the model simulations presented here are only approximates since the true values of the porous media bulk density ρ and volumetric water content θ have not yet been directly measured. These parameters have been currently estimated using nonreactive tracer BTC. The true values of ρ and θ will be determined when all displacement experiments are completed and the column can be destroyed.

RESULTS AND DISCUSSION

The transport of nonreactive Br in undisturbed soil columns from the midslope and bottom swale regions of the field site were investigated at a variety of moisture contents (Figs. 2 and 3). These experiments were conducted to evaluate the utility of the unsaturated set-up (Fig. 1) and to quantify solute dispersion and time-dependent mass-transfer processes through these soils. Breakthrough curves (BTC) for the nonreactive tracers were increasingly asymmetric with increased saturation, which is indicative of enhanced preferential flow. Tailing of the BTC became less significant during unsaturated conditions because of a decrease in pore class heterogeneity involved in the transport process. Effluent tracer concentrations were modeled with the convective-dispersive (CD) equation (Figs. 2 and 3), with optimization of the dispersion coefficient and revealed significant solute mass-transfer limitations among pore classes during transport at 0 cm tension (saturation). The classical CD equation could not describe the extended tailing of the observed data at this tension, and a modified version of the CD equation was required that considered solute mass-transfer limitations into immobile pore domains (not shown). Mass-transfer limitations became increasingly negligible with 10 and 15 cm tension (unsaturated) because macropore flow was eliminated (Figs. 2 and 3). The classical CD equation was found to adequately describe observed effluent concentrations for these unsaturated conditions. Tracers studies using a variety of moisture contents are useful for quantifying processes important to in-situ contaminant mobility during transient storm events.

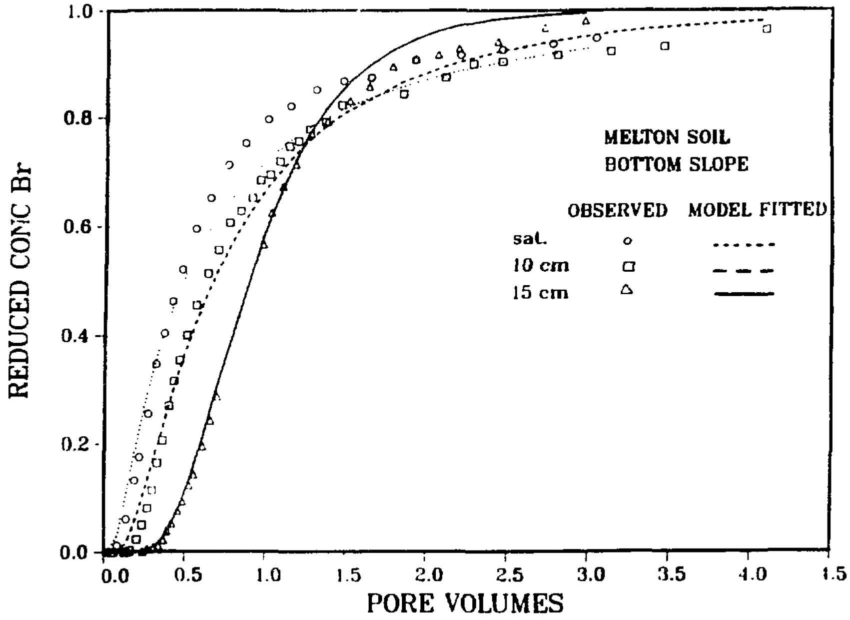

Figure 2. Observed Br effluent concentrations at three tensions on a bottom slope soil with model fitted curves using the classical convective-dispersive equation.

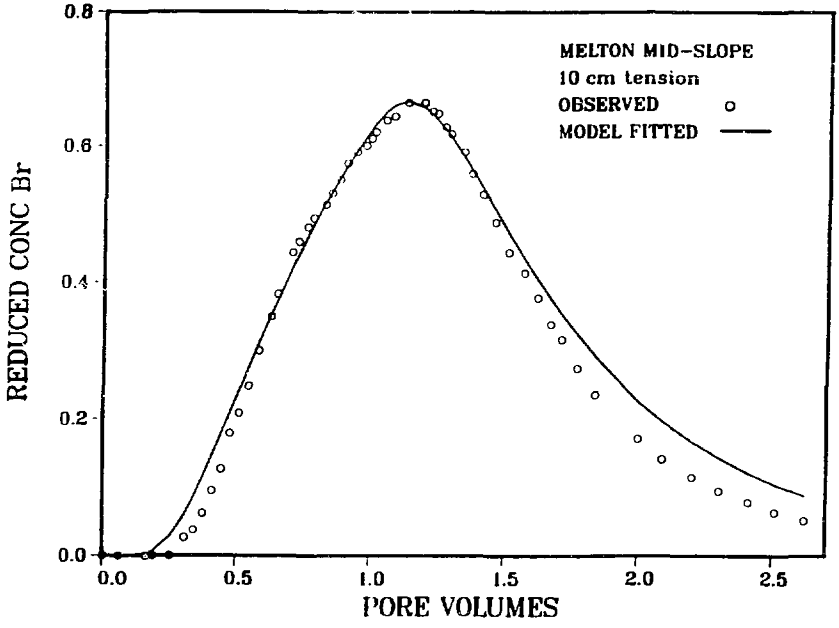

Figure 3. Observed Br effluent concentrations at 10 cm tension on a midslope soil with a model fitted curve using the classical convective-dispersive equation.

The transport of reactive Sr^{2+} and Co^{2+} (Figs. 4 and 5, respectively) in the undisturbed soil column from the midslope of the field site were investigated at 10 cm tension in order to closely mimic the natural unsaturated flow characteristics in this soil. The breakthrough of Sr and Co in this column required about 5-6 months for each independent experiment. Observed BTCs for the Sr and Co tracers were delayed relative to the nonreactive Br BTC indicating that the former tracers were adsorbed by the soil (Figs. 3-5). Effluent concentrations of Sr and Co were modeled with the classical CD equation (equilibrium model) using independent measurements of all model parameters with estimates of solute retardation ($R=1+\rho k_d/\theta$ where k_d is the solute distribution coefficient) obtained using batch techniques (Figs. 4 and 5, solid lines). The model simulated curves described the overall trends of the observed data yet slightly overpredicted the true transport of these solutes. Deviations between the observed and model predicted curves may be the result of inaccurate estimates of ρ and θ for this particular column. Since displacement experiments are currently being performed on this column, direct measurement of these parameters is not possible until the column can be destroyed. Nevertheless, nonequilibrium mass-transfer considerations did not appear necessary for these binary systems (i.e. Sr-Ca, Co-Ca) at this tension. The consideration of kinetics did not improve model simulations of observed Sr transport (Fig. 4) and only slightly improved the model description of observed Co transport (Fig. 5). Earlier investigations have shown that saturated transport of reactive inorganic solutes in this soil exhibit significant mass-transfer limitations (Jardine et al. 1988).

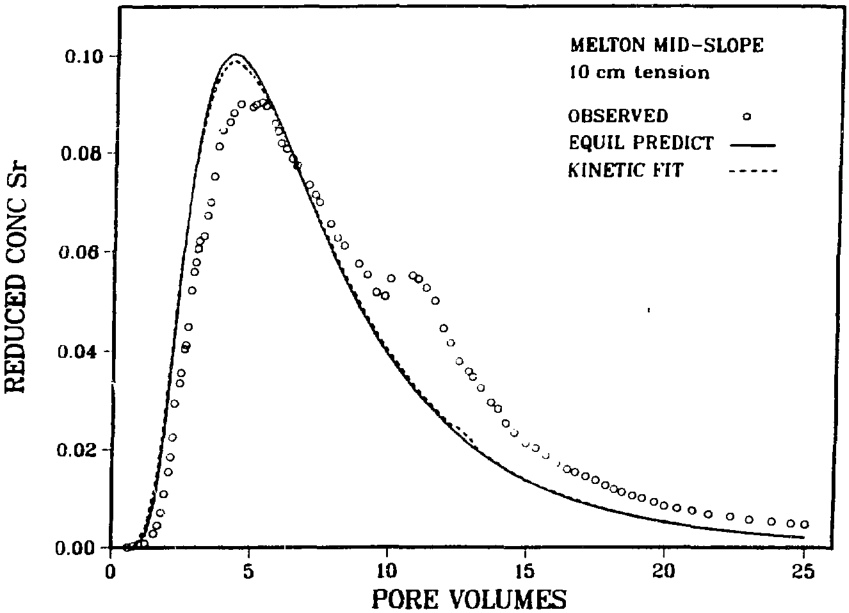

Figure 4. Observed Sr^{2+} effluent concentrations at 10 cm tension on a midslope soil with a model predicted curve using the convective-dispersive equation and independently measured model parameters.

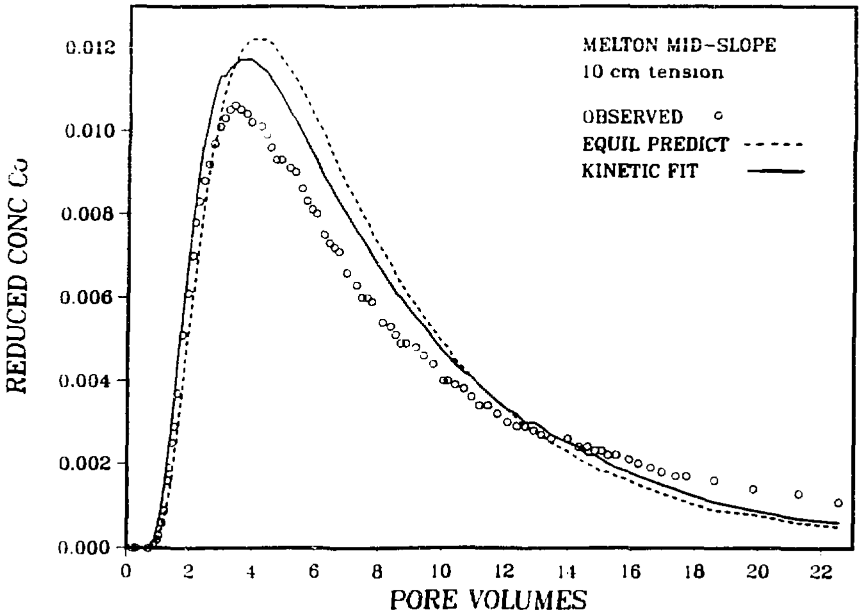

Figure 5. Observed Co^{2+} effluent concentrations at 10 cm tension on a midslope soil with a model predicted curve using the convective-dispersive equation and independently measured model parameters.

In order to understand the thermodynamic processes governing cation transport in these soils, Sr-Ca and Co-Ca equilibrium adsorption isotherms were determined on subsamples of disaggregated soil obtained near the soil column (Figs. 6 and 7). These isotherms were used to model Sr and Co transport in the undisturbed soil columns as previously discussed. Isotherms were determined on samples that included and excluded saprolitic material. The isotherms were nearly linear and support the use of the transport model to predict Sr and Co mobility in this soil (Figs. 4 and 5).

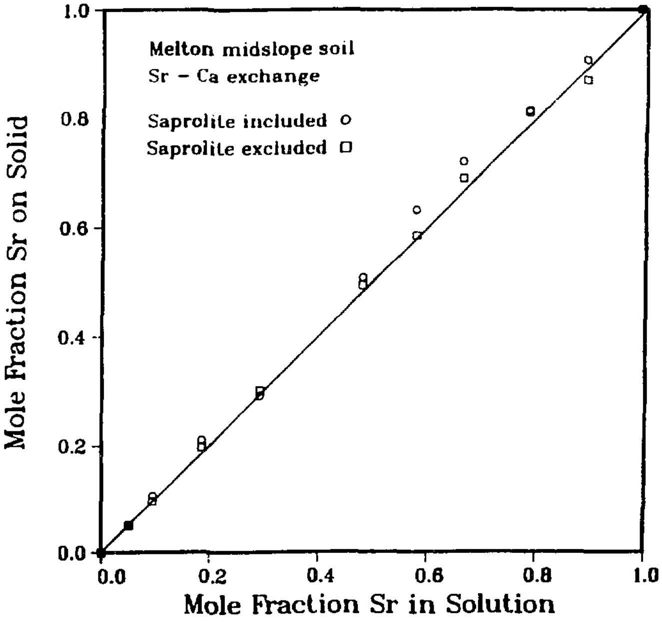

Figure 6. Equilibrium adsorption isotherms for Sr^{2+}-Ca^{2+} exchange on midslope soil including and excluding saprolite at I=0.003, pH=5.6, and 298K.

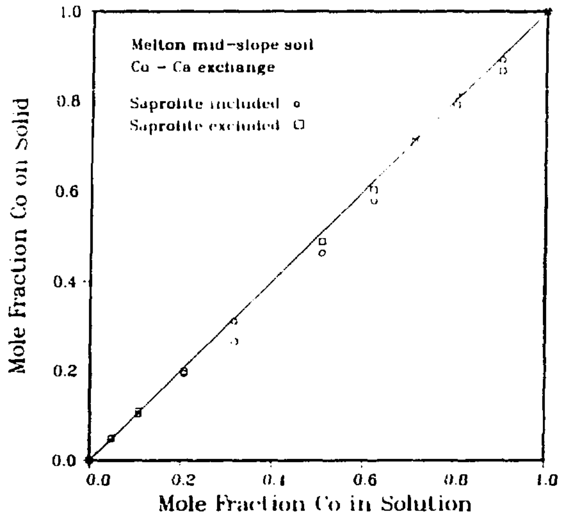

Figure 7. Equilibrium adsorption isotherms for Co^{2+}-Ca^{2+} exchange on sidslope soil including and excluding saprolite at $I=0.003$, pH=5.6, and 298K.

The isotherms were essentially identical for samples including and excluding disaggregated saprolite. The former sample had a slightly greater cation exchange capacity (CEC) of 14.4 cmol+/kg relative to samples excluding saprolite which had a CEC of 13.5 cmol+/kg. The similarity is convenient for modeling purposes since it is unknown what fraction of the porous media, if any, is excluded from cation exchange reactions with mobile Sr and Co. The exchange reactions of Sr, Co, and Ca on this soil are nearly ideal, however Sr is slightly more preferred to Ca, with the latter slightly preferred to Co (i.e. Sr>Ca>Co). The 1:1 diagonal (solid lines Figs. 6 and 7) indicate the non-preferential adsorption isotherm.

Both miscible displacement and shake batch methods were utilized to quantify the cation exchange equilibria relationships. Isotherms obtained by the two methods were essentially identical with slope values (k_d-distribution coefficient) being very similar (Figs. 8 and 9). Retardation values (R) determined by the batch methods were similar to the R values obtained via optimization of the CD equation to observed Sr and Co BTC (Table 1). Values of CEC obtained from the R values are shown for convenience. These results suggest that preferential transport of reactive tracers is negligible for the unsaturated conditions used in this study and that the massive saprolite within the soil is a chemically active constituent during reactive solute transport.

Comparison of retardation values and cation exchange capacities from adsorption isotherms and those model fitted from unsaturated column displacement studies

System	Column[*]	Shake batch[#]	Miscible Displacement[#]
	R		
Sr-Ca	8.7	7.8	7.1
Co-Ca	7.3	8.4	7.5
	CEC (cmol+ kg^{-1})		
Sr-Ca	14.3	14.5	13.3
Co-Ca	12.2	14.0	13.0

[*] Best fit using equilibrium CD model to column displacement expt.
[#] Assumes $\rho = 1.6\ cm^3/g$ and $\theta = 0.32\ cm^3/cm^3$.

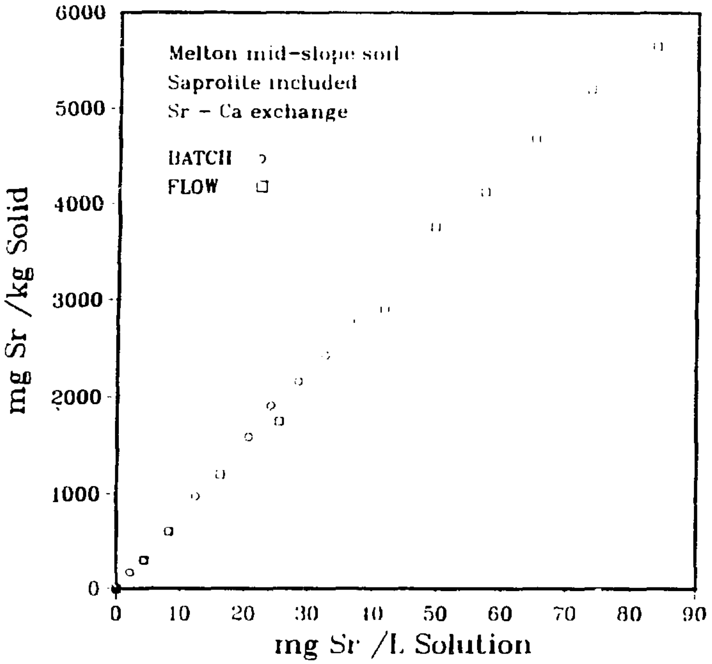

Figure 8. Equilibrium adsorption isotherms of Sr^{2+}-Ca^{2+} exchange on midslope soil including saprolite for shake batch and miscible displacement methods at I=0.003, pH=5.6, and 298K.

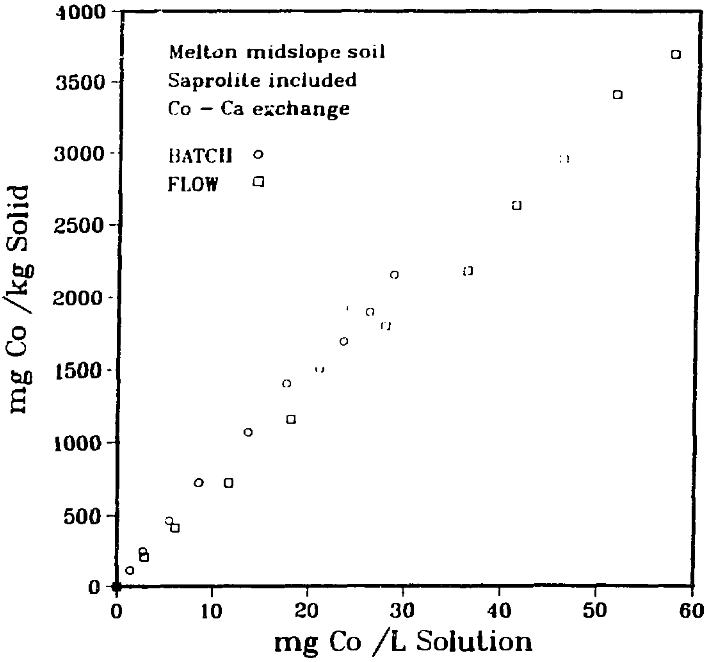

Figure 9. Equilibrium adsorption isotherms of Co^{2+}-Ca^{2+} exchange on midslope soil including saprolite for shake batch and miscible displacement methods at I=0.003, pH=5.6, and 298K.

CONCLUSIONS

The thermodynamic and kinetic processes controlling the transport of Sr, Co, and Ca in unsaturated, heterogeneous soils have been investigated. Using realistic unsaturated conditions, the transport of Sr and Co in the presence of Ca does not appear to be limited by time-dependent mass transfer. The exchange reactions of these cations on this soil are nearly ideal, however Sr is slightly more preferred to Ca, with the latter slightly preferred to Co (i.e. Sr>Ca>Co). Retardation values for Sr and Co on soil determined from batch methods were similar to retardation values determined for Sr and Co effluent concentrations from unsaturated soil columns. This suggest that preferential flow is negligible in the unsaturated soil column and that the massive saprolite within the soil is a chemically active constituent during reactive solute transport. Since the transport studies have been performed using realistic unsaturated, undisturbed soils, these results have direct implications on modeling in-situ subsurface contaminant transport. The key hydrologic and chemical factors which influence solute mobility in these soils can be used to parameterize and calibrate field scale subsurface contaminant transport models. This process is the first step towards successful deterministic field scale model validation.

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