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DETERMINATION OF TRANSPORT PARAMETERS FROM STEP AND PULSE DISPLACEMENT OF CATIONS AND ANIONS

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ABSTRACT

Although transport problems in the field usually involve a number of solute species, which react in different ways with the soil, most experimental work considers displacement in binary systems where the two solutes are either non-reactive or obey a particular exchange isotherm. This study reports theoretical and experimental findings for displacement involving up to four solutes.

Experimentally determined breakthrough curves (BTC's) are reported for pulse and step inputs, using Ca, K, Na, Br, and Cl as solutes. Although several methods were used to determine the coefficient of longitudinal dispersion, D, and the retardation factor, R, the most attention was given to the use of time moments.

Theoretical moments were derived from analytical solutions of the advection-dispersion equation, ADE, in the Laplace domain to investigate dispersion and retardation for pulse inputs. Solutions of the ADE for a first- and a third-type boundary condition at the inlet were used for a non-layered and a two-layer medium.

Step displacement experiments were conducted in various media with layering transverse to the direction of flow. No increased dispersion was found as a result of layering. Pulse displacement experiments were carried out in homogeneous soils for binary systems, a

NaCl-pulse in a $CaBr_2$-saturated medium, and for ternary systems, a pulse of K and Na in a Ca-saturated medium. The moment method was used to determine values for D and R. The accuracy of the experiments was found to be acceptable, based on various mass balances and the electroneutrality principle. Values for D, obtained from anion displacement experiments and measured cation exchange isotherms, were used to numerically predict BTC's for cations. The role of non-linear exchange was investigated by comparing experimental (non-linear exchange) with theoretical (linear exchange) moments. Non-linear exchange was shown to have a large influence on the value of D, in particular for Na. The average pulse spread, determined by experimental moments, resulting from hydrodynamic dispersion and non-linear exchange, was in a number of instances five times the average pulse spread determined by theoretical moments, based only on hydrodynamic dispersion.

INTRODUCTION

Transport of dissolved chemicals in porous media has been studied quite extensively in order to predict the fate of contaminants and agricultural chemicals in soils. Such transport has traditionally been described with the advection-dispersion equation (ADE) under the assumption that the transport and flow properties are uniform with respect to time and position. It is now widely recognized, however, that under field conditions these properties can vary in time and space *(22)*. Therefore, deterministic approaches to model transport will generally result in poor predictions of the fate of contaminants. Various other methods to predict flow and transport have consequently been employed, emphasizing the stochastic nature of transport and flow *(6)* or abandoning any mechanistic description of the processes involved *(11)*.

Accepting the validity of the ADE under laboratory conditions, the transport parameters to quantify the advective and dispersive flux need to be known. A number of techniques are currently in use to determine these transport parameters from experimental data. It should be noted that in the older literature considerable attention was given to the determination of D, assuming Fickian dispersion. Although this assumption is incorrect for a number of situations, and even if it were correct, it implies that the average solute displacement is unaltered by dispersion. The value for R quantifies interactions between solute and solid phase, which can greatly affect average solute displacement. In order to predict the average location of the solute front, the value for R is of more importance than D.

Techniques of determining D and R are based on relatively simple analytical solutions, graphical methods, or fitting experimental data with theoretical (non-equilibrium) models *(e.g., 24)*. In particular, curve fitting techniques are quite popular. As pointed out by Parker and van Genuchten *(13)*, uniqueness problems might arise if too many unknown factors have to be considered to fit experimental concentration profiles with theoretical solutions. In addition, the models used to describe transport can not be properly validated with curve fitting alone *(15)*.

A method commonly used in chemical engineering to analyze experimental BTC's is the method of moments *(e.g., 16)*, although it has also been used in hydrology *(9)* and to some extent in soil science *(19)*. Values for D and R can be determined in a straightforward way using time moments of the BTC. The method was originally used for advection-dispersion problems by Aris *(2)*. The total amount of solute, the mean breakthrough time, and the degree of spreading and tailing are easily obtained by determining various time moments of the BTC.

Our first main objective concerned the determination of transport parameters. First, some well known methods were evaluated using experimentally determined BTC's. Second, some simple ways to determine an effective retardation factor were investigated. Third, the method of moments was used to characterize spreading and retardation for various BTC's.

Aris *(3)* showed how analytical solutions of transport equations in the Laplace domain can be used to obtain those moments theoretically. Solutions are more easily obtained in the Laplace domain than in the regular space-time domain. These solutions allow D and R to be determined from results of solute transport experiments. From a theoretical point of view, the technique can be used to obtain explicit expressions for retardation factors and dispersion coefficients for a particular transport model. Valocchi *(21)* applied the technique to aggregated media in order to evaluate the validity of the local equilibrium assumption and to predict spreading and tailing of the BTC.

Theoretical moments can also be used to study the effects of layering and the type of inlet condition on the transport of a solute pulse. Our understanding of transport in heterogeneous media, as most field soils are, might be enhanced by resorting to a relatively simple medium such as a collection of uniform soil layers perpendicular to the direction of flow *(18)*. Regarding the effect of the type of inlet boundary condition on the determination of D and R, van Genuchten and Parker *(23)* showed that for flux- and volume-averaged concentrations a first- and a third-type condition should be used, respectively. If the results for a first- and third-type condition are similar, depending on the values of D and v, one might prefer the use of the simpler first-type condition.

Our second main objective was to derive theoretical moments based on the ADE. First, these moments were used to obtain experimental values for D and R. Second, theoretical moments were determined for transport in a two-layer medium, with the interface perpendicular to the direction of flow to demonstrate the effect of soil heterogeneity on breakthrough time, spreading, and tailing. Third, theoretical moments were derived based on a first- and a third-type inlet condition. Again, this condition applies to both the inlet of a homogeneous medium and individual layers of a layered medium.

Knowledge of the relationship between the solute concentration in the adsorbed and solution phase is necessary to solve the transport equation. In the case of transport of a non-linearly exchanging solute, advection and dispersion terms depend on the concentration and composition of solutes. Current methods used to determine transport parameters do not account for this dependency because it is assumed that the exchange is linear. This greatly simplifies the mathematical solution of the transport equation. Although the assumption of linearity is a convenient one, it is quite often not a realistic one.

Furthermore, the total amount of adsorbed cations depends on the composition of the adsorbed cations. This affects the value of R. Differences in the apparent cation exchange capacity (CEC) were reported to be particularly large between Ca and Na soils *(12)*. Simultaneous cation and anion displacement experiments are helpful in detecting changes in the total amount of solute. The latter is accomplished using a mass balance for each individual ion as well as total cation and anion balances. In binary systems with a constant total electrolyte level, only one concentration can be chosen independently. In ternary systems with a constant total electrolyte level, the concentration of a particular cation depends on the two other cation concentrations. This dependency allows us to illustrate the difference in behavior of a favorably and an unfavorably exchanging, incoming cation.

Our third main objective was to investigate the influence of ion exchange on transport and to determine transport parameter values using a pulse displacement. First, BTC's were determined in binary systems by applying a NaCl pulse to a $CaBr_2$ medium. Second, BTC's were determined for a Na/K pulse applied to a Ca medium. Third, theoretical moments for experiments with assumed linear exchange were compared with experimental moments resulting from experiments with obvious non-linear exchange.

THEORY

Formulation of the Transport Equation

One-dimensional transport of a reactive solute species during steady flow in a homogeneous porous medium may be described by:

$$\frac{\rho_b}{\theta}\frac{\partial S}{\partial t} + \frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \qquad (1)$$

where ρ_b is the dry bulk density of the medium $[ML^{-3}]$, θ is the volumetric water content $[L^3L^{-3}]$, S is the mass of solute in the adsorbed phase per mass of solid $[MM^{-1}]$, t is time [T], C is the solute concentration in the liquid phase $[ML^{-3}]$, D is the effective dispersion coefficient $[L^2T^{-1}]$, x is the distance in the direction of flow [L], and v is the average pore water velocity $[LT^{-1}]$. It should be noted that Eq.(1) is commonly rewritten as

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \tag{2}$$

where R is the dimensionless retardation factor given by:

$$R = 1 + \frac{\rho_b}{\theta} \frac{\partial S}{\partial C} \tag{3}$$

Persaud and Wierenga *(14)* discussed the influence of the slope of the exchange isotherm, $\frac{\partial S}{\partial C}$, on solute transport. This slope depends, among other things, on the concentrations of solutes present. The experimental determination of exchange isotherms is usually carried out assuming that the sums of the solute concentrations in both the liquid and the adsorbed phases are constant, no hysteresis occurs in the exchange reaction, and the reactions reach instantaneous equilibrium. In the case of linear exchange, the slope of the isotherm is constant and equal to the well known distribution coefficient K_d $[L^3M^{-1}]$. The retardation factor is then constant as well, which greatly simplifies the mathematical solution of the ADE. For non-linear exchange, a constant value for R can be used by considering an effective K_d value *(e.g., 20)*.

If physical non-equilibrium exists, the liquid phase is often partitioned into a "mobile" and an "immobile" region. Solute transport in the mobile region occurs by advection and dispersion, whereas the amount of solute present in the immobile region is determined by diffusive transport between the mobile and immobile region of the liquid phase. Transport in the medium is now described by *(13)*:

$$(\theta_{mo} + f\rho_b K_d)\frac{\partial C_{mo}}{\partial t} + (\theta_{im} + (1-f)\rho_b K_d)\frac{\partial C_{im}}{\partial t} = \theta_{mo} D_{mo}\frac{\partial^2 C_{mo}}{\partial x^2} - v\theta\frac{\partial C_{mo}}{\partial x} \quad (4)$$

$$(\theta_{im} + (1-f)\rho_b K_d)\frac{\partial C_{im}}{\partial t} = \alpha\,(C_{mo} - C_{im}) \quad (5)$$

where the subscripts mo and im refer to mobile and immobile regions of the liquid phase, respectively; f represents the fraction of exchange sites that equilibrates with the mobile liquid phase; and α is a first order rate constant, which determines the diffusive transfer of solute between mobile and immobile regions $[T^{-1}]$. Note that $\theta_{mo}+\theta_{im}=\theta$ and $\theta_{im}C_{im}+\theta_{mo}C_{mo}=\theta C$. Furthermore, we assumed that the exchange process for mobile and immobile exchange sites is governed by the same distribution coefficient.

Although our mathematical analysis concerns equilibrium transport of a non-reactive solute (R=1), it is easily extended to linearly exchanging solutes by replacing v and D with v^* (=v/R) and D^* (=D/R), respectively. The transport problem posed is subject to the following conditions and assumptions: (1) the medium is initially free of the displacing solute, (2) for the inlet boundary, both the concentration- or first-type and the flux- or third-type condition will be used, (3) the medium is semi-infinite in order to formulate the outlet condition, and (4) both step and pulse type displacement will be used. These conditions and assumptions can be mathematically described as:

$$C(x,t) = 0 \qquad 0<x<\infty \qquad t=0 \qquad (6\text{-a})$$

$$C(x,t) = f(t) \qquad \text{(first-type)} \qquad x=0 \qquad t>0 \qquad (6\text{-b})$$

$$\left(-D\frac{\partial C}{\partial x} + vC\right)\bigg|_{x=0} = vf(t) \qquad \text{(third-type)} \qquad t>0 \qquad (6\text{-c})$$

$$\text{with } f(t) = \begin{cases} C_o & 0<t<t_o \\ 0 & \text{otherwise} \end{cases} \qquad (6\text{-d})$$

$$\frac{\partial C}{\partial x}\bigg|_{x\to\infty} = 0 \qquad t>0 \qquad (6\text{-e})$$

For the step type displacement t_o approaches infinity, whereas for the pulse type displacement t_o is finite. Figure 1 schematically illustrates the two types of experiments for displacement in a soil column with length L, assuming a first-type inlet boundary condition. The inlet concentration, C_{in} at x=0, as well as the outlet concentration, C_{out} at x=L, are shown as a function of time. For D=0,the BTC is the same as the input curve. Also shown is front spreading due to Fickian dispersion. Non-linear exchange will alter the shape of the BTC, depending on the nature of the exchange isotherm.

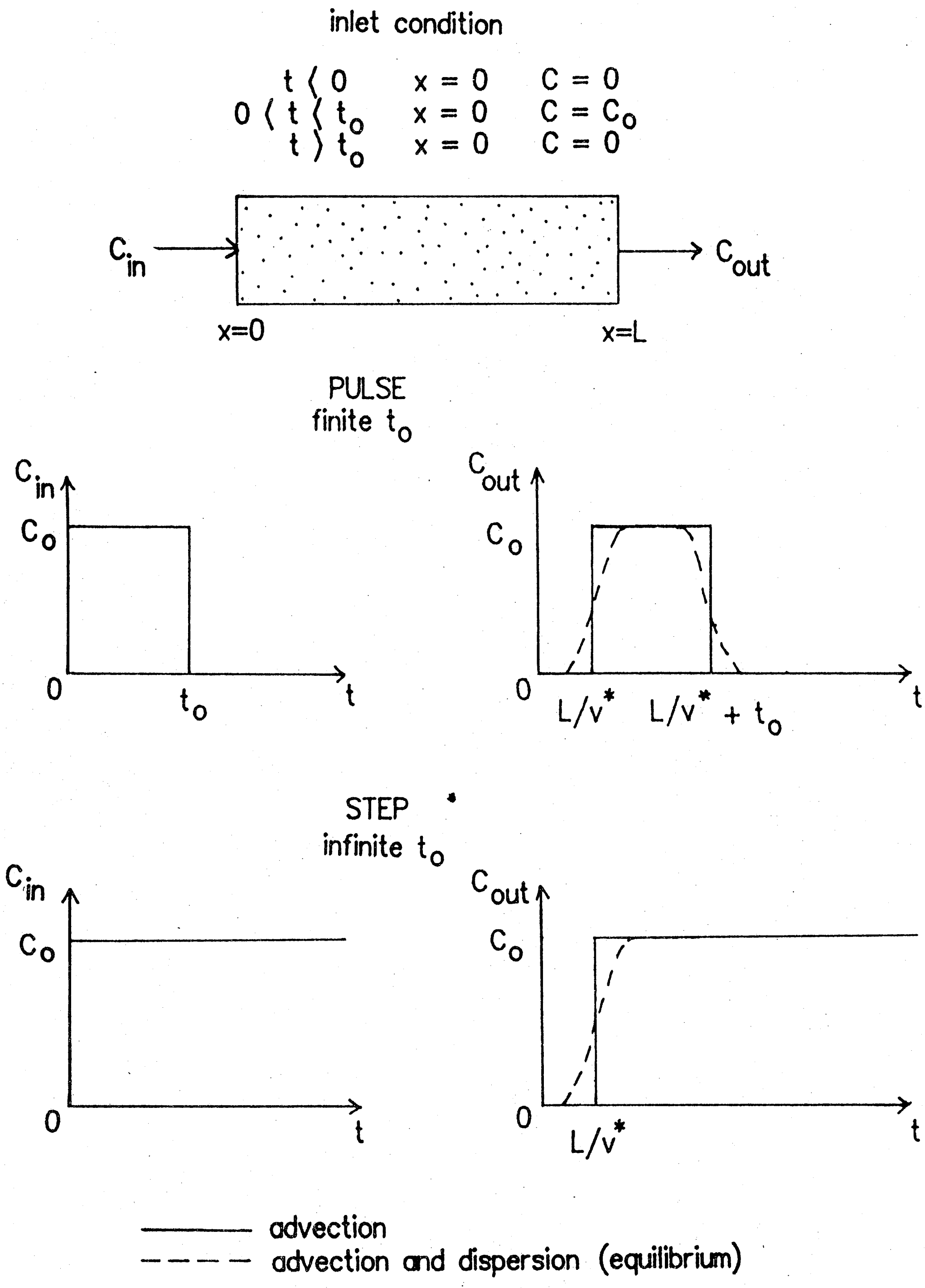


FIG. 1. Schematic representation of solute displacement experiments with step and pulse input.

Methods to Determine Transport Parameters Reported in the Literature

First, the method described by Fried and Combarnous *(7)* was used. This method utilizes a simplified solution of Eq.(2) via transformation into a diffusion type of equation, subject to a first-type inlet condition for a step input. For a non-reactive solute the following solution applies:

$$C(x,t) = \frac{C_o}{2}\, \mathit{erfc}\left[\frac{x-vt}{\sqrt{4Dt}}\right] \qquad (7)$$

The concentration profile obeys a normal distribution function. The coefficient of dispersion can then be obtained from the BTC according to:

$$D = \frac{1}{8}\left[(x-vt_{0.16})/\sqrt{t_{0.16}} - (x-vt_{0.84})/\sqrt{t_{0.84}}\right] \qquad (8)$$

where $t_{0.16}$ and $t_{0.84}$ denote the time at which C/C_o equals 0.16 and 0.84, respectively.

Second, the simplified solution given by Eq.(7) can be used to determine an explicit relationship between D and C(x,t). This technique, first used by Rose and Passioura *(17)* was generalized by van Genuchten and Wierenga *(24)*, who expressed Eq.(7) in terms of the following dimensionless variables:

$$T = vt/L \qquad (9)$$

$$P = vL/D \qquad (10)$$

where L is the length of the soil column [L], T is the number of pore volumes leached through the column, and P is the column Peclet number.

For a non-reactive solute, the following expression was derived for the column outlet:

$$\mathit{inverfc}(2\frac{C}{C_o}) = \frac{P^{1/2}}{2}\left[\frac{1-T}{T^{1/2}}\right] \approx -\frac{P^{1/2}}{2}\,\ln T \qquad (11)$$

Plotting the dimensionless exit concentration, $C_e = C/C_o$, on probability paper as a function of $\ln T$ should yield a straight line (see figure 44-9, *24*). The slope α, of the curve $\mathit{inverfc}(2C_e)$ versus $\ln T$, is obtained by determining the value for $\mathit{inverfc}(2C_e)$ at two points which are sufficiently far apart. The following relationship between P and α was used:

$$P = 4\alpha^2 - \Delta \qquad (12)$$

where Δ is a correction factor. For further details, including the determination of R, as well as values for Δ, one is referred to the Chapter by van Genuchten and Wierenga *(24)*.

Third, transport parameters in this study were determined with the program CXTFIT, which fits analytical solutions of Eq.(2) or Eq.(4) and (5) to observed concentration distributions obtained by step and pulse displacement. The program, based on a least-squares inversion method, was described by Parker and van Genuchten *(13)*.

Graphical Determination of R for Step and Pulse Input

The determination of an effective retardation factor, assuming zero dispersion and physical equilibrium, is illustrated schematically in figure 2 for a pulse input, with concentration C_o and duration t_o, into a column of length L. The soil solute concentration, ρ_s, expressed as mass of solute in the liquid phase per volume of medium, is plotted as a function of position at various times.

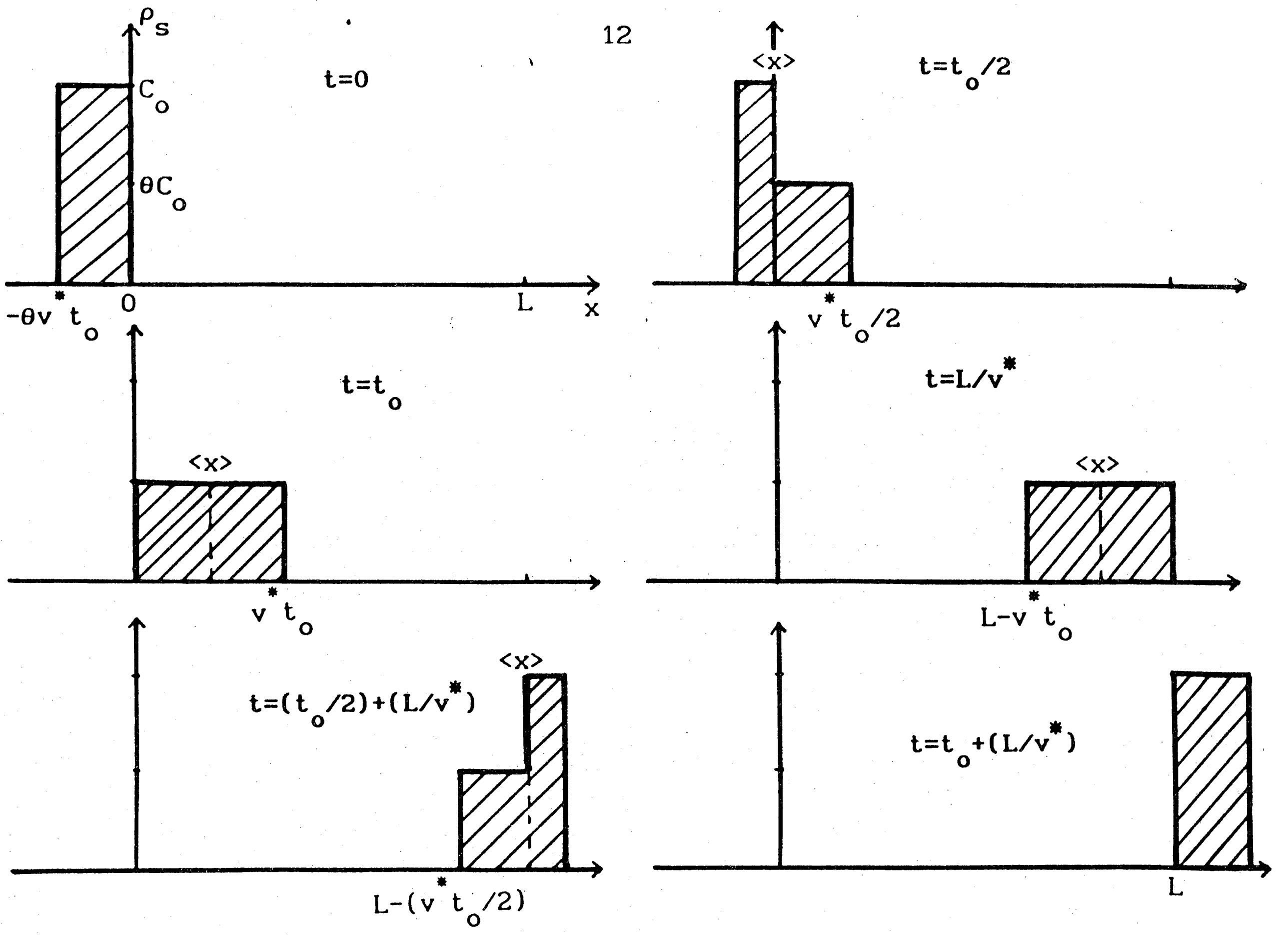


FIG. 2. Hypothetical concentration distribution as a function of position at various times for a pulse input.

The velocity of a linearly exchanging solute, v^*, is equal to v/R, whereas for a non-reactive solute, the velocity, $v^*=v$, is equal to the velocity of the solvent. From the average position of the pulse, <x>, it can be seen that the mean residence time is equal to L/v^* and that its mean breakthrough time, $\bar{t}$, is equal to $(L/v^*) + (t_o/2)$. The retardation factor, R, is the ratio of the mean residence time for solute and solvent, respectively. This allows the determination of R from BTC's either graphically (this section) or with the method of moments (next section). An effective value for R can be obtained for non-linearly exchanging solutes provided that the effluent concentration reaches a maximum concentration C_o prior to complete displacement of the pulse.

For most displacement experiments v is known, while for the solute $\bar{t}$ can be obtained from the experimentally determined BTC. In the case of a pulse displacement, R is determined according to:

$$R = \frac{\bar{t}_{solute} - (t_o/2)}{(L/v)} \tag{13}$$

The determination of $\bar{t}$ for the solute is illustrated in figure 3, which shows an arbitrary BTC for a pulse input. A value for $\bar{t}$ can be obtained via graphical or mathematical integration, satisfying the condition that areas A and B are equal.

A similar method can be employed for a step type displacement. The average residence time of the front, $\bar{t}$, is equal to the average breakthrough time and can be obtained graphically as illustrated in figure 3. Using the step displacement, the retardation factor follows from:

$$R = v\bar{t}/L \tag{14}$$

A very useful concept in BTC-analysis of a step input is that of column holdup *(4)*. The column holdup, H, can be defined as:

$$H = \frac{v}{L}\int_0^\infty (1 - \frac{C}{C_o})\, dt \tag{15}$$

where C is the concentration of the displacing solute in the effluent. According to Eq.(15), H is the total amount of resident solute exiting the column. In case the column is saturated with the displacing solute ($t\to\infty$), H is the total amount of solute that was present in the column at t=0.

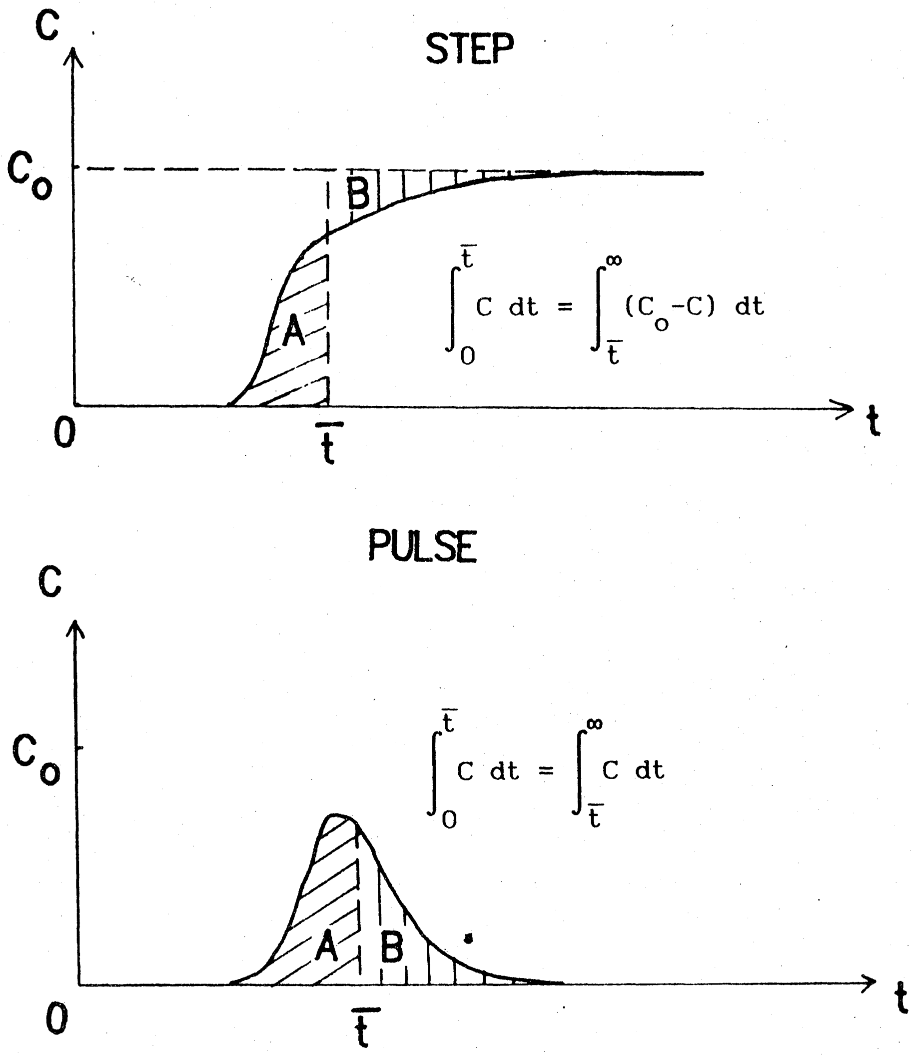


FIG. 3. Determination of the mean breakthrough time based on BTC's with step and pulse type input.

The column holdup is obtained rather easily from BTC data. The relationship between H and R can be established from known analytical solutions of the ADE. For conditions given by Eq. (6), the following expressions were found *(24)*:

$$R = \begin{cases} H & \text{(first-type)} \\ H(1 + (D/vL))^{-1} & \text{(third-type)} \end{cases} \tag{16}$$

Determination of Transport Parameters with the Moment Method

The last method to be discussed for determining transport parameters is the moment method, which is applicable to BTC's in response to a pulse feed. The p-th time moment, m_p, of a concentration distribution C(x,t), at a given location, is given by:

$$m_p(x) = \int_0^\infty t^p \, C(x,t)\, dt \qquad p = 0,1,2,.... \tag{17}$$

The first, second, third, and fourth moments of the concentration distribution can be used to characterize the mean, variance, skewness and kurtosis, respectively, of the BTC. Moments can also be used to characterize spatial distributions of the concentration *(8)*. From the time moments one can obtain absolute moments, defined by:

$$\mu'_p(x) = \frac{m_p(x)}{m_0(x)} = \int_0^\infty t^p \, C(x,t)\, dt \;/\; \int_0^\infty C(x,t)\, dt \tag{18}$$

and central moments, defined by:

$$\mu_p(x) = \frac{1}{m_0(x)} \int_0^\infty (t-\mu'_1(x))^p \, C(x,t)\, dt \tag{19}$$

Since the ADE was used to describe transport, we are particularly interested in the use of the moment method to characterize advective and dispersive transport.

The first absolute moment, $\mu'_1(x)$, represents the mean breakthrough time for the pulse at column position x. As was already discussed, the ratio of the mean residence times of solute and solvent in the columns can be used to determine an effective value for R. For an arbitrary pulse in a column with length L, one can formally write:

$$R = \frac{(\mu_1'(L) - \mu_1'(0))_{solute}}{(\mu_1'(L) - \mu_1'(0))_{solvent}} \tag{20}$$

which is a more general expression than Eq.(13). According to figure 2, $\mu_1'(0)=t_o/2$ for both the solvent and the solute for a pulse input. Furthermore, the mean residence time for the solvent is determined by the average pore water velocity; the denominator of Eq.(20) is therefore equal to L/v. At this point the only unknown in Eq.(20) is $\mu_1'(L)$, which can be obtained with the BTC using Eq.(17) and (18).

It is convenient to obtain the BTC as a function of dimensionless time T (the number of pore volumes leached through the column), in which case the p-th moment is defined as:

$$M_p = \int_0^\infty T^p \, C(x,T) \, dT \qquad p=0,1,2,.... \tag{21}$$

Replacing m_p by M_p, the following expression for R can be found according to Eqs.(18) and (20):

$$R = \frac{M_1}{M_0} - \frac{T_o}{2} \tag{22}$$

where the pulse duration is now expressed as T_o pore volumes.

The second central moment, $\mu_2(x)$, is a measure of the average pulse spread relative to the mean breakthrough time, $\mu_1'(x)$:

$$\mu_2(x) = \frac{1}{m_0} \int_0^\infty (t-\mu_1')^2 \, C(x,t) \, dt \tag{23}$$

Application of Eq.(17) allows Eq.(23) to be written as

$$\mu_2(x) = \mu_2' - (\mu_1')^2 \tag{24}$$

The question then arises how experimentally determined moments of the BTC can be used to quantify the transport parameters D^* and v^* (and hence R). The answer lies in the determination of moments based on the theoretical solutions of the transport equation. For instance, for a Dirac type of initial condition in an infinite medium the solution of the ADE, assuming Fickian dispersion, can be found with the help of Eq.(2-6) of Crank *(5)*. Substituting the solution into Eq.(17) and evaluating the appropriate integrals leads to the following theoretical expressions:

$$\mu_1'(x) = \frac{xR}{v} + \frac{2DR}{v^2} \tag{25-a}$$

$$\mu_2(x) = \frac{2DxR^2}{v^3} + 8\left[\frac{DR}{v^2}\right]^2 \tag{25-b}$$

Equating these theoretical expressions for $\mu_1'(x)$ and $\mu_2(x)$ with their experimental values, obtained from the BTC with the use of Eq.(18) and (24), enables the subsequent determination of R and D for a known value of v. The determination is facilitated if the BTC is determined at two positions, x_1 and x_2, in the medium. The retardation and spreading between these points can be characterized by:

$$\mu_1'(x_2)-\mu_1'(x_1) = (x_2-x_1)\frac{R}{v} \tag{26-a}$$

$$\mu_2(x_2)-\mu_2(x_1) = (x_2-x_1)\,\frac{2DR^2}{v^3} \tag{26-b}$$

The value for R is obtained from Eq.(26-a), whereas the value for D follows from Eq.(26-b) using this R value.

However, in many cases the determination of moments by substituting the appropriate solution for C(x,t) into Eq.(17) is not a feasible approach. In the next section, a relatively simple method to determine time moments will therefore be discussed.

Theoretical Determination of Moments According to Aris

Aris *(3)* showed how time moments can be determined from a solution for the concentration in the Laplace domain, $\bar{C}(x,s)$. For a theoretical BTC in the Laplace domain, the p-th moment of the concentration distribution is given by:

$$m_p(x) = (-1)^p \lim_{s \to 0} \left[\frac{d^p}{ds^p} \bar{C}(x,s) \right] \qquad p = 0,1,2,... \qquad (27)$$

The solution $\bar{C}(x,s)$ depends on the mathematical model used to describe transport. This model is not necessarily restricted to the ADE. Because it is generally easier to obtain $\bar{C}(x,s)$ than $C(x,t)$, the use of moments is convenient to determine transport parameters for more complicated transport models *(e.g., 21)*. By equating a sufficient number of experimentally determined moments obtained from a particular BTC using Eq.(17) to theoretical moments obtained according to Eq.(27), the transport parameter values of the chosen mathematical model can be determined.

We will consider the two inlet conditions (6-b) and (6-c) for a homogeneous medium and for a medium consisting of two layers with a well defined interface at $x=L_1$. Formulation of the problem and details of the solution procedure are presented in Appendix A, while the analytical solutions are given in table 1. The first layer of the two-layer medium has the same properties as the homogeneous one-layer medium. Although it was assumed that R=1, the analysis can be extended to reactive solutes by using v^* $(=v/R)$ and D^* $(=D/R)$ instead of v and D. With these solutions, time moments were determined according to Eq.(27), as well as absolute moments according to Eq.(18) and central moments according to Eq. (19).

Table 1. Solutions of the ADE in the Laplace Domain for a One- and a Two-layer System with a First- and Third-type Inlet Condition

Case	Layer	Condition	Solution
A	1	first	$\bar{f}\ \mathit{exp}(\lambda_1 x)$
B	1	third	$\frac{v_1 \bar{f}}{v_1 - D_1 \lambda_2}\ \mathit{exp}(\lambda_1 x)$
C	2	first	$\bar{f}\ \mathit{exp}(\lambda_1 L_1 + \lambda_2 (x - L_1))$
D	2	third	$\frac{\theta_1}{\theta_2} \frac{\bar{v}_1 f}{v_2 - D_2 \mu_2}\ \mathit{exp}(\lambda_1 L_1 + \lambda_2 (x - L_1))$

$\bar{f}$, λ_1 and λ_2 are defined in Appendix A and the subscripts $_1$ and $_2$ denote first and second layers, respectively.

The procedure to determine these time moments is briefly outlined in Appendix B, while the resulting expressions for moments up to order three are presented in Appendix C. We will discuss the effects of the inlet condition and layering on R and D in terms of these results.

The time moments most commonly used in BTC analysis are μ_1' and μ_2 *(10)*. The expressions for μ_1' and μ_2 for the four cases listed in table 1 are given in table 2.

The effect of the inlet condition can be evaluated by comparing case A and B:

$$\text{Breakthrough time : } (\mu_1')_B - (\mu_1')_A = \frac{D_1}{v_1^2}$$

$$\text{Spreading : } (\mu_2)_B - (\mu_2)_A = 3 \frac{D_1^2}{v_1^4}$$

Table 2. Expressions for μ'_1 and μ_2 for Transport in a One- and a Two-layer Medium Subject to a First- and a Third-type Condition

case	μ'_1	μ_2
A	$\frac{t_o}{2} + \frac{x}{v_1}$	$\frac{t_o^2}{12} + 2\,\frac{xD_1}{v_1^3}$
B	$\frac{t_o}{2} + \frac{x}{v_1} + \frac{D_1}{v_1^2}$	$\frac{t_o^2}{12} + 2\,\frac{xD_1}{v_1^3} + 3\,\frac{D_1^2}{v_1^4}$
C	$\frac{t_o}{2} + \frac{L_1}{v_1} + \frac{x-L_1}{v_2}$	$\frac{t_o^2}{12} + 2\,\frac{L_1D_1}{v_1^3} + 2\,\frac{(x-L_1)D_2}{v_2^3}$
D	$\frac{t_o}{2} + \frac{L_1}{v_1} + \frac{x-L_1}{v_2} + \frac{D_2}{v_2^2}$	$\frac{t_o^2}{12} + 2\,\frac{L_1D_1}{v_1^3} + 2\,\frac{(x-L_1)D_2}{v_2^3} + 3\,\frac{D_2^2}{v_2^4}$

It appears that breakthrough time and spreading increase for a third-type condition compared to a first-type condition. This will be referred to as the "inlet effect."

The effect of layering will be evaluated by comparing case B and D, i.e., for a third-type condition, assuming that $v_1=v_2$. At the interface we'll let x approach L_1 from $x>L_1$, i.e., $\lim_{x\downarrow L_1}$. Comparing the first absolute moment and the second central moment for case B and D we get:

$$\text{Breakthrough time}: \quad (\mu'_1)_D-(\mu'_1)_B = \frac{1}{v^2}\,(D_2-D_1) = \lim_{x\downarrow L_1}\left[(\mu'_1)_D-(\mu'_1)_B\right]$$

$$\text{Spreading}: \quad (\mu_2)_D-(\mu_2)_B = \frac{2(x-L_1)}{v^3}\,(D_2-D_1) + \frac{3}{v^4}\,(D_2^2-D_1^2)$$

$$\lim_{x\downarrow L_1}\left[(\mu_2)_D-(\mu_2)_B\right] = \frac{3}{v^4}\,(D_2^2-D_1^2)$$

The difference in μ'_1, indicative for the effect of layering on the breakthrough time, can be viewed as the inlet effect for layer two, D_2/v_2^2, minus the inlet effect for layer one, D_1/v_1^2. As soon as the pulse enters layer two, the contribution of the inlet effect for layer one will disappear. The breakthrough time in the two-layer medium can therefore be derived from the breakthrough times in two homogeneous media which have the same properties as the two layers. The fact that an interface is present does not influence the breakthrough time. To investigate whether layering introduces additional spreading, a similar approach can be followed. Differences in μ_2 for the one- and two-layer medium are caused by the "inlet effect", $3D^2/v^4$. It appears that there is no particular "interface effect", the inlet effect for the first layer is substituted by an inlet effect for the second layer at the interface.

As mentioned earlier, theoretical moments can be used to determine transport parameters. These moments depend on the physical model chosen to describe solute transport. The expressions in Appendix C were based on the ADE, applicable to equilibrium transport with a constant R value, but other models could be used as well. Additional transport parameters, for more complicated transport models, can also be determined using theoretical moments and experimental data. It should finally be noted that expressions for these moments also depend on the mathematical model, i.e., the conditions at the interface, chosen to describe solute transport.

MATERIALS AND METHODS

Four types of studies were conducted to study the problems outlined in the introduction. First, a pilot study was carried out with homogeneous soils to get acquainted with experimental procedures and to evaluate the reliability of various techniques. Second, step-type displacement experiments were carried out in layered soils with binary exchange. The third and fourth study involved pulse-type displacement for a binary system (different cations and anions) and a ternary system (three different cations) in a homogeneous soil.

The experimental setup is illustrated in figure 4. Cylindrical plexiglass columns of 15 or 30 cm length, with an internal diameter of 6 cm, were used for the displacement studies. The plexiglass cylinders were enclosed by plexiglass endcaps. A piece of cheese cloth was placed in each end cap to prevent loss of soil during the experiments. Each column was carefully packed with air dried soil that had first been passed through a 2-mm sieve and subsequently through another sieve to obtain the desired size fraction. Soil types and their taxonomic classification are listed in table 3. All soils are subsoils, which were collected at Alabama Agricultural Experiment Station research units. The dry soil weight and volume for each column were determined

Table 3. Classification of Soils

Soil series	Family description
Dothan	Fine-loamy, siliceous, thermic Plinthic Paleudults
Wickham	Fine-loamy, mixed, thermic Typic Hapleudults
Savannah	Fine-loamy, siliceous, thermic Typic Fragiudults
Lucedale	Fine-loamy, siliceous, thermic Rhodic Paleudults
Troup	Loamy, siliceous, thermic Grossarenic Paleudults

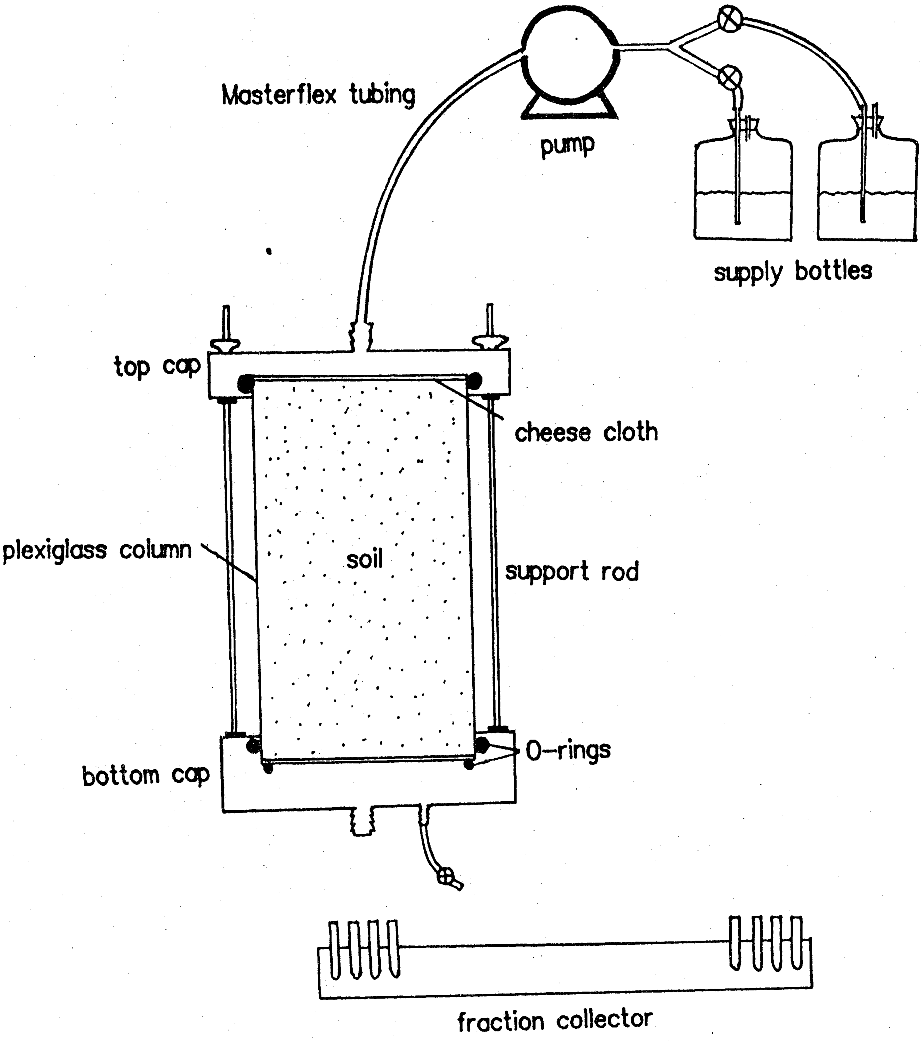


FIG. 4. Schematic of experimental setup.

gravimetrically to determine porosity, ε, and dry bulk density, ρ_b. The soil was then slowly saturated from the bottom with water containing a specific solute with concentration C_o. In the pilot study, a constant head device (Mariotte bottle) was used to apply the solution. However, substantial variations in flow rate occurred. The Mariotte bottle device was, therefore, replaced with a Masterflex constant volume pump (Cole-Parmer, Chicago, Illinois) in all later studies.

After saturating the soil from the bottom and establishing steady outflow, the columns were inverted to obtain vertical downward flow. Solute concentrations of the effluent and, occasionally, of the eluent were monitored to verify whether or not the soil was saturated with the particular solute. Upon saturation with the resident solute, the input line was switched, at time t=0, to the reservoir containing the displacing solute(s). It is noted that the volume of solution in the lines was kept at a minimum. Effluent solutions were collected in test tubes by means of a fraction collector (Buchler, Fort Lee, New Jersey). No tubing was used at the column outlet. For the pulse-type displacement, the supply line was switched back to the original solution at time t_o. At the end of each experiment, the weights of the (saturated) soil column and air dry soil were determined to obtain effective values for the volumetric water content and the pore volume. The flow rate during the experiment was determined gravimetrically at regular time intervals. Various solutes were used in the experiments, namely Ca, Na, or K as cations and Cl or Br as anions. Ca and K concentrations were determined with the ICAP, whereas Na concentrations were determined with flame emission spectrophotometry. The Cl and Br concentrations were determined with the HPLC.

RESULTS AND DISCUSSION

Pilot Study

BTC's for the pilot study are shown in figures 5 to 10, with the experimental conditions given in table 4. In the figures, DBD and VWC denote ρ_b and θ. Al figures show the dimensionless concentration as a function of dimensionless time (T=vt/L). The first two experiments involved the displacement of a 0.1 *M* $CaCl_2$ solution from a Troup soil by solute free water. The BTC's are rather steep and symmetrical. Breakthrough of the front for $C/C_o=0.5$ occurred after sligthly more than one pore volume, indicating that some of the Ca was present as an "adsorbed" phase.

Table 4. Experimental Conditions for Solute Displacement During Pilot Study

Experiment #	Soil	Size fraction	Solute Res.	Solute Dis.	ρ_b	θ	v	PV
		µm			g cm^{-3}		cm d^{-1}	cm^3
1	Troup	250-500	$CaCl_2$	-	1.91	0.28	1304.6	175
2	Troup	250-500	$CaCl_2$	-	1.92	0.28	1208.2	173
3	Lucedale	<840	$CaCl_2$	$CaBr_2$	1.58	0.40	17.8	251
4	Lucedale	<840	$CaCl_2$	$CaBr_2$	1.59	0.40	67.8	249
5	Wickham	<500	$CaCl_2$	$CaBr_2$	1.43	0.46	8.61	286
6	Wickham	500-1000	$CaCl_2$	$CaBr_2$	1.29	0.52	262.7	321

L = 30.6 cm.
Res. and Dis. denote resident and displacing solute, respectively, and PV is pore volume.

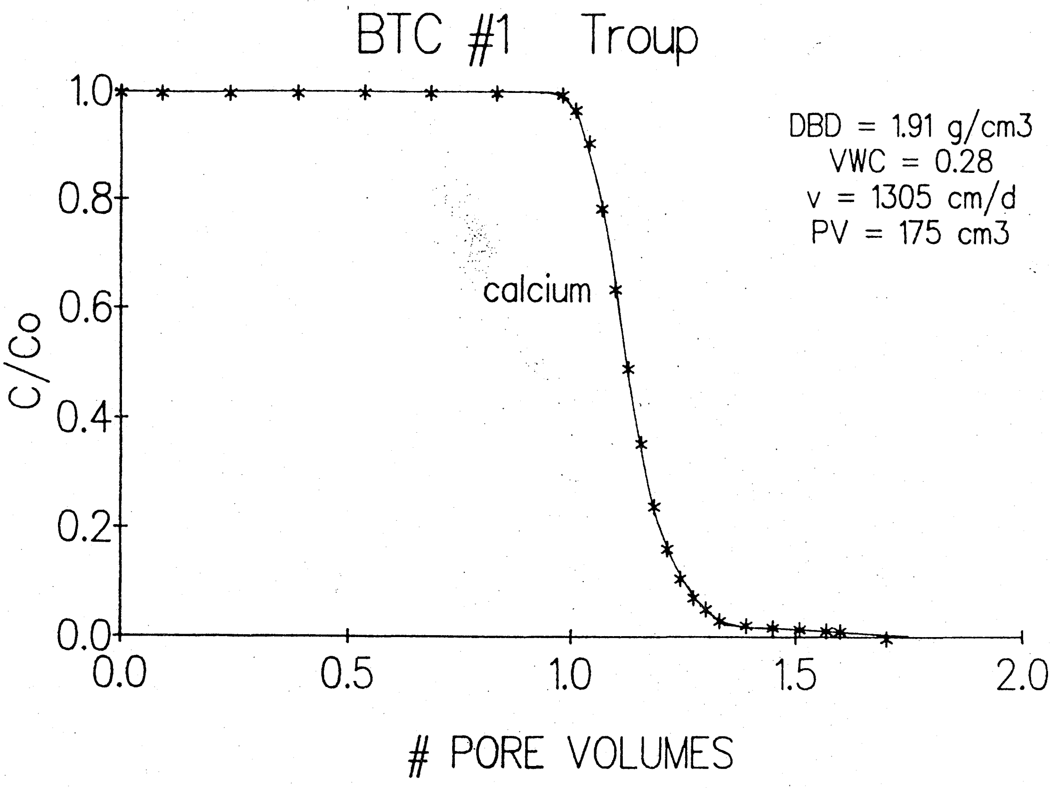


FIG. 5. BTC #1: Ca curve for Troup soil.

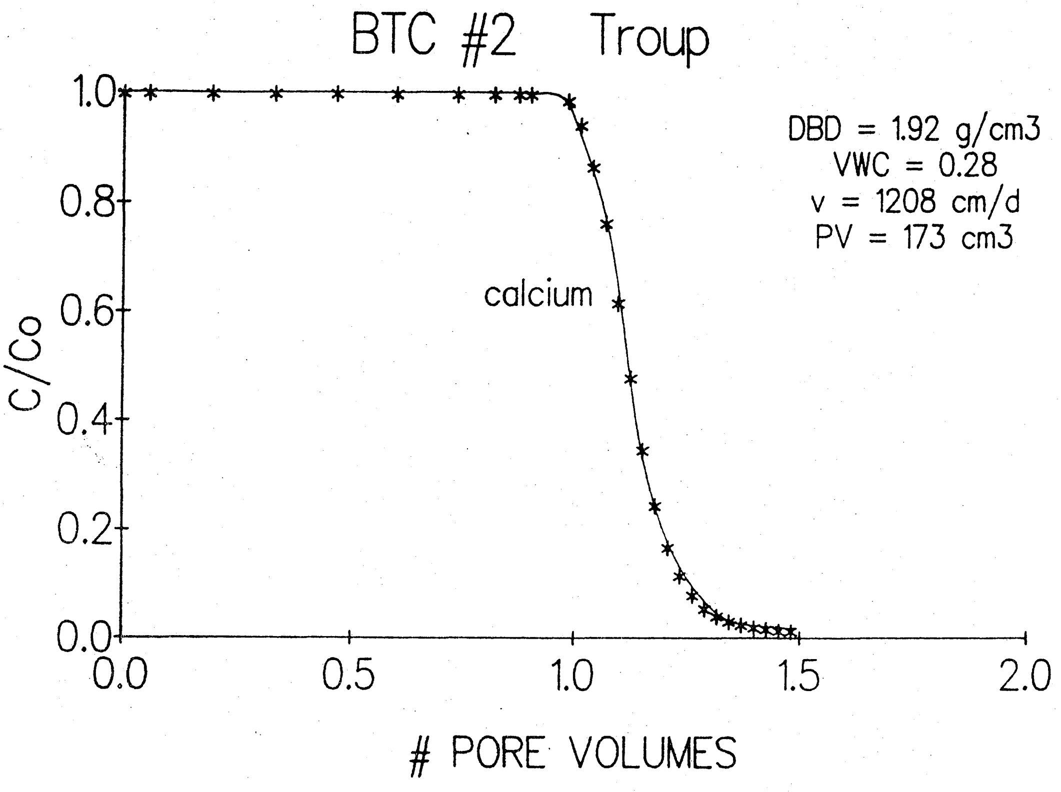


FIG. 6. BTC #2: Ca curve for Troup soil.

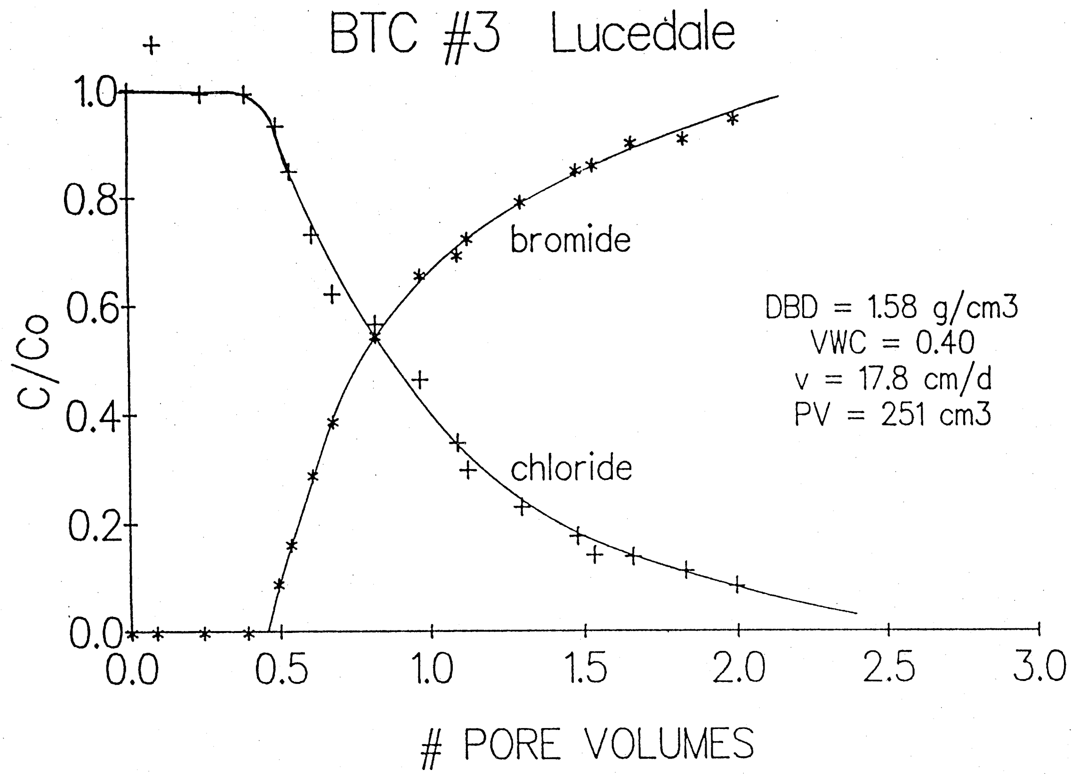


FIG. 7. BTC #3: Br and Cl curves for Lucedale soil.

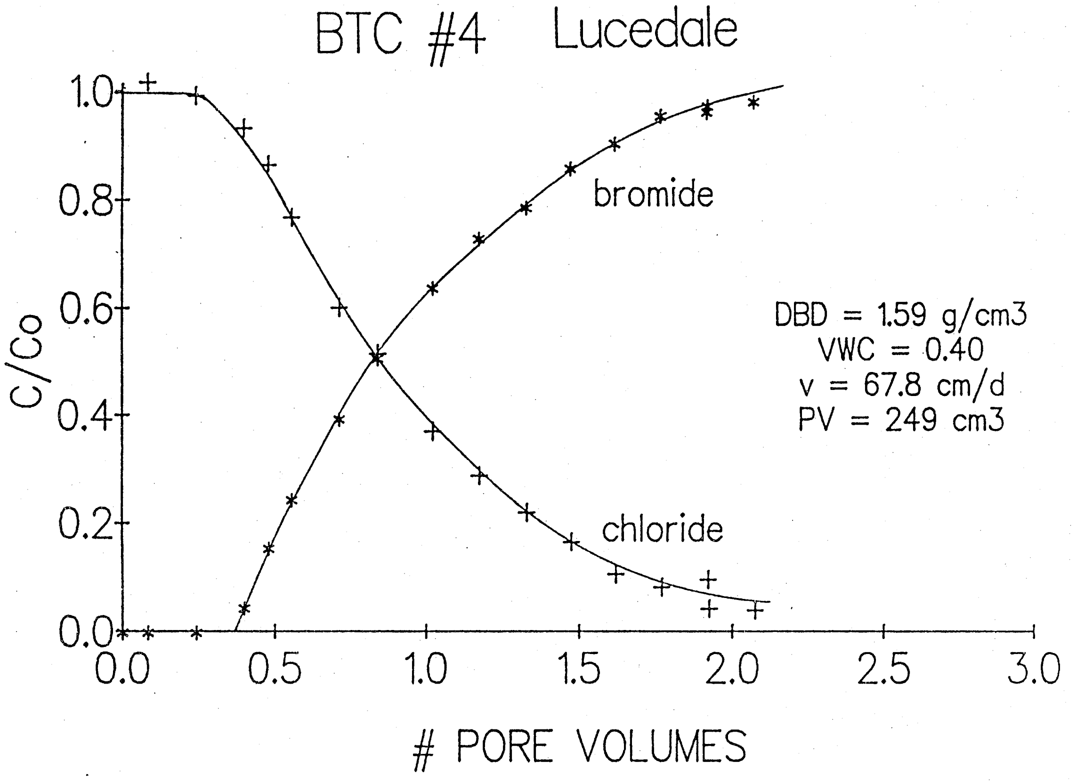


FIG. 8. BTC #4: Br and Cl curves for Lucedale soil.

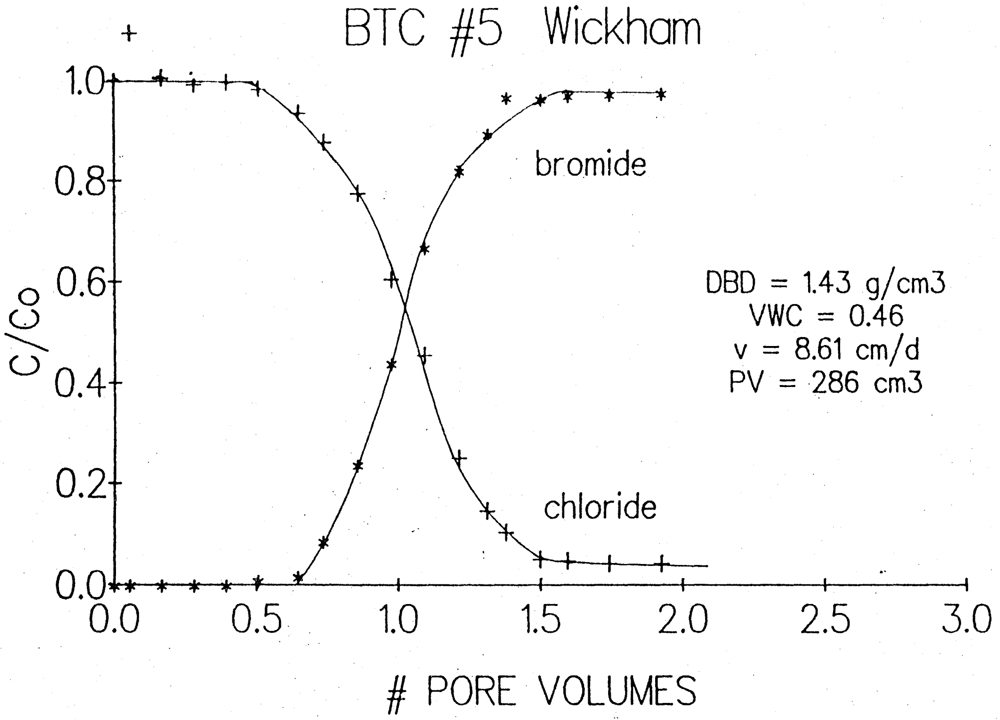


FIG. 9. BTC #5: Br and Cl curves for Wickham soil.

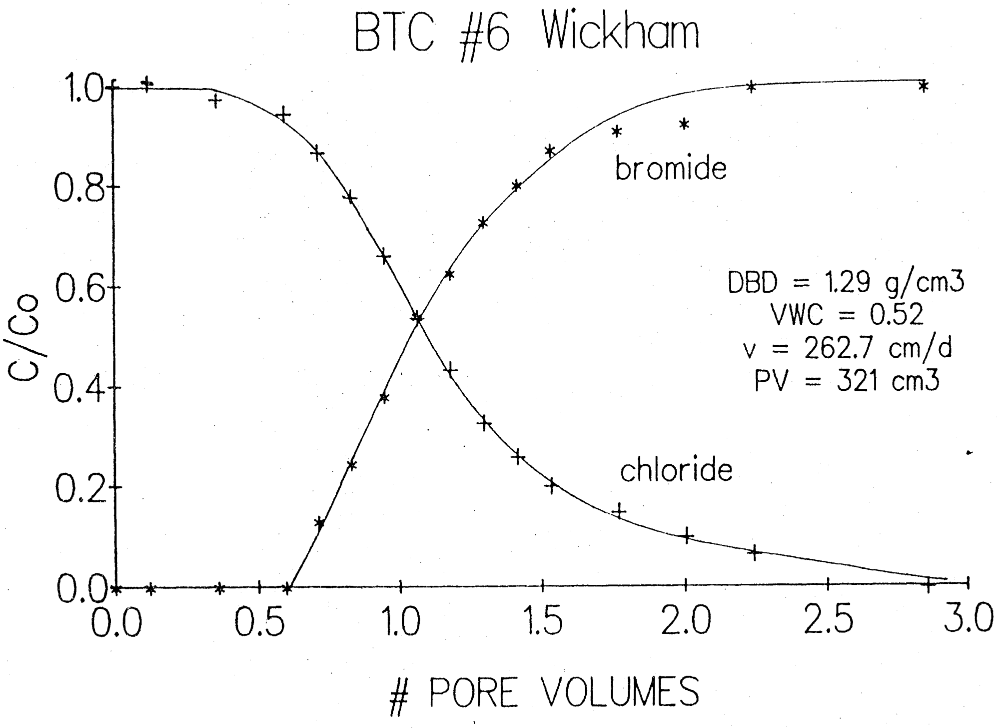


FIG. 10. BTC #6: Br and Cl curves for Wickham soil.

Figures 7 to 10 show the results for the displacement of 0.01 *M* $CaCl_2$ by 0.01 *M* $CaBr_2$. Both Cl and Br concentrations in the effluent were determined. The BTC's were not symmetrical about C/C_o=0.5 for the Lucedale soil, suggesting that non-equilibrium conditions existed. The Wickham soil exhibits a more symmetric front, particularly at the lower value for v (figure 9). For these experiments, breakthrough generally occurred before one pore volume had passed, indicating the possibility of anion exclusion. However, variations in flow rate were observed, which affected the reliability of the number of pore volumes actually leached through the column. As mentioned earlier, a constant volume pump was used in later studies and the outflow rate was determined at frequent intervals.

The transport parameters for experiments 1 to 6 were first determined with some of the methods obtained from the literature (i.e., based on Eq.(7)). Table 5 contains the results obtained using Eq.(8),

Table 5. Determination of Dispersion Coefficients According to Fried and Combarnous (7)

Experiment #	Solute	$t_{0.16}$	$t_{0.84}$	v	D
		d	d	cm d^{-1}	cm^2 d^{-1}
1	Ca	0.025	0.029	1304	104.1
2	Ca	0.026	0.030	1208	70.7
3	Cl	0.928	2.647	17.8	76.7
	Br	0.865	2.690	17.8	90.4
4	Cl	0.230	0.668	67.8	303.4
	Br	0.225	0.693	67.8	338.5
5	Cl	2.772	4.514	8.61	7.87
	Br	2.914	4.371	8.61	5.14
6	Cl	0.089	0.204	262.7	712.9
	Br	0.088	0.176	262.7	483.4

Table 6. Determination of Dispersion Coefficients Using $\mathit{inverfc}(2C_e) = \alpha\ \ell n T + \beta$†

Experiment #	Solute	α	P	D	$C_e(P)$	R
				$cm^2 d^{-1}$		
1	Ca	-9.640	370.7	107.6	0.50	1.12
2	Ca	-9.589	366.8	100.5	0.50	1.12
3	Cl	1.322	5.99	90.9	0.50	0.92
	Br	-1.267	5.43	100.5	0.50	0.83
4	Cl	1.333	6.11	339.7	0.50	0.83
	Br	-1.405	6.90	300.8	0.50	0.83
5	Cl	2.746	29.2	9.03	0.49	1.05
	Br	-3.295	42.4	6.21	0.48	1.00
6	Cl	1.710	10.7	751.5	0.50	1.11
	Br	-2.132	17.2	468.3	0.50	1.04

† Semi-infinite medium, third-type condition, $0.1<C<0.9$ *(24)*.

whereas table 6 shows the results derived using Eq.(12). The slope α was determined by plotting $C_e=C/C_o$ as a function of *ℓn* T on probability paper.

To determine transport parameters via curve fitting, the concentrations of resident and displacing anions were expressed as $(C_o-C)/C_o$ and C/C_o, respectively. The input files, containing the BTC's, for these experiments as well as all later experiments are listed in Appendix D. Table 7 contains parameters obtained with the program CXTFIT assuming equilibrium and physical non-equilibrium conditions. Comparing the results obtained with the methods based on Eq.(7) and the results from CXTFIT, it appears that D determined by the first method (table 5), and D and R determined by the second method (table 6), are of the same magnitude as D and R determined by the curve fitting procedure assuming physical equilibrium (table 7). Insight into

Table 7. Determination of Transport Parameters Using CXTFIT *(13)*

#	Solute	CDM†	Holdup		Equilibrium		Non-equilibrium				
			H	R	D	R	θ_{mo}	θ_{im}	α	D	R
					cm^2d^{-1}				d^{-1}	cm^2d^{-1}	
1	Ca	r		1.155	105.4	1.127	0.28	0.00	1620	97.5	1.121
		f	1.158	1.158	105.3	1.130	0.28	0.00	2630	97.4	1.124
2	Ca	r		1.210	98.0	1.125	0.28	0.00	1863	89.0	1.118
		f	1.213	1.213	97.9	1.128	0.27	0.01	4.09	57.4	1.131
3	Cl	r		0.851	88.9	0.878	0.20	0.20	0.38	2.65	1.030
		f	0.983	0.983	84.5	1.026	0.34	0.06	24.9	87.3	1.046
	Br	r		0.823	78.6	0.817	0.24	0.16	0.26	8.25	0.943
		f	0.936	0.936	75.0	0.938	0.40	0.00	∞	70.4	0.901
4	Cl	r		0.795	377.0	0.839	0.21	0.29	1.52	73.7	0.955
		f	0.931	0.931	354.8	0.996	0.22	0.28	1.49	85.5	0.989
	Br	r		0.814	328.0	0.820	0.17	0.23	2.26	0.96	0.946
		f	0.935	0.935	309.5	0.952	0.17	0.23	2.26	0.99	0.947
5	Cl	r		1.002	8.71	1.034	0.46	0.00	∞	8.04	1.016
		f	1.035	1.035	8.57	1.068	0.00	0.46	4.43	0.63	1.060
	Br	r		1.010	6.13	0.998	0.46	0.00	∞	5.76	0.981
		f	1.033	1.033	6.06	1.021	0.00	0.46	33.0	5.00	1.019
6	Cl	r		1.123	719.1	1.108	0.45	0.07	0.49	496.2	1.208
		f	1.220	1.220	694.9	1.209	0.34	0.18	∞	703.9	1.216
	Br	r		1.067	508.5	1.051	0.52	0.00	∞	470.0	1.026
		f	1.133	1.133	495.6	1.118	0.52	0.00	∞	495.6	1.118

† Concentration Detection Mode: r=resident, f=flux-averaged.
\# is experiment number.

the nature of the exchange process can be gained from examining the solute retardation. For the Troup soil (#1 and 2), R is slightly over 1, indicating that only a minor part of the displaced Ca was adsorbed, as would be expected for the high initial solute concentration (0.1 *M*) and sandy soil texture. For the Lucedale soil (#3 and 4) R<1, implying that anion exclusion occurred. In contrast, some retardation of the anion took place for the Wickham soil (#5 and 6), possibly due to adsorption by Fe-oxides.

In examining the equilibrium versus non-equilibrium results (table 7), it should be noted that the values for D according to the equilibrium model are generally higher than those based on the non-equilibrium model. This supports the idea that part of the spreading can be explained on the basis of non-equilibrium.

It seems reasonable to assume that transport parameters determined for Cl and Br by the same model should be approximately equal for a given soil column if the anions are non-reactive. However, especially for experiment 4, very different D values were found for Cl and Br using the non-equilibrium model. The values for θ_{mo} and θ_{im} also show considerable differences. Experiment 6 can serve as an example; if Cl is the tracer, the model predicts the existence of both mobile and immobile regions in the liquid phase, whereas $\theta_{im}=0$ for Br. These discrepancies may have been caused by poor initial estimates of the transport parameters in the program CXTFIT and the high number of unknowns (i.e., five), which can create uniqueness problems. For the equilibrium model, the values for D are very much the same for Cl and Br. It appears that fitting data with the non-equilibrium model does not necessarily provide reliable parameters. The equilibrium model was, therefore, used in the remaining part of this study, although non-equilibrium conditions might have existed in some cases.

The holdup, according to Eq.(15), was determined from the BTC using the trapezoidal rule. In a number of cases, the BTC was extrapolated to asymptotically approach $C/C_o=1$ to "ensure" complete displacement. The results are included in table 7. Subsequently, values for R were determined according to Eq.(16), using "equilibrium"

D values for a third-type condition. The values for R based on H correspond roughly to those found by the other methods. The discrepancies between values for R for experiments 3 and 4, obtained with H using a first- and a third-type condition, can be attributed to the low values of the column Peclet number (cf. Eq.(16)).

Transport in Layered Media with Binary Exchange

The experimental conditions for the displacement studies in layered media are listed in table 8. The soil materials possessed a wide variety of chemical and physical properties. Note that $\bar{v}$, $\bar{\theta}$, and $\overline{PV}$ are averaged over all layers. $\overline{PV}$ and $\bar{\theta}$ were found from the difference in wet and dry weight of the column. The Darcy flux and $\bar{v}$, assuming steady flow, were obtained by determining the amount of effluent over time.

Table 8. Experimental Conditions for Solute Displacement in Layered Media

Experiment #	Soil	Depth	ρ_b	ε	$\bar{\theta}$	$\bar{v}$	$\overline{PV}$
		cm	g cm^{-3}			cm d^{-1}	cm^3
11	Troup	0-12.5	1.64	0.38			
	Savannah I	12.5-17.5	1.37	0.48	0.38	132.63	232.7
	Troup	17.5-30	1.67	0.36			
12	Dothan I	0-15	1.60	0.39	0.334	102.48	201.0
	Dothan II	15-30	1.29	0.51			
13	Troup	0-15	1.65	0.38	0.317	140.2	191.4
	Lucedale II	15-30	1.42	0.47			

I : <250 μm.
II : 500-840 μm.

$\overline{PV}$ is mean pore volume of combined layers.

Resident solution : 0.01 *M* KBr.
Displacing solution : 0.005 *M* $CaBr_2$.

The resulting BTC's are shown in figures 11 to 13. The K concentration decreases after a number of pore volumes has passed, indicating that considerable retardation of Ca occurred. These curves appear to be fairly symmetrical; the data were fitted with CXTFIT using the equilibrium model, to determine D and R. The fitted parameters and r^2, quantifying correlation between fitted and experimental curves, are given in table 9. It appears that an excellent fit was obtained, yielding values for the transport parameters which were averaged over the layers. This illustrates that curve fitting can produce seemingly reliable values, when in fact no physical basis exists to determine D and R from matching a theoretical (based on a homogeneous soil) with an experimental BTC for a layered medium. Also included in table 9 are values for R based on H using a first- and third-type condition. It should be noted that H is equal to R for a first-type condition. The correspondence between the retardation factors obtained with curve fitting and column holdup is excellent.

Table 9. Determination of Transport Parameters for Step Displacement in Layered Media with CXTFIT and Column Holdup

#	Solute	D† [cm^2d^{-1}]	R†	r^2	R‡ Condition First	R‡ Condition Third
11	Ca	57.858	4.120	0.996	4.136	4.077
	K	60.513	4.088	0.996	4.208	4.145
12	Ca	55.266	10.884	0.998	10.881	10.688
	K	53.667	10.818	0.996	11.072	10.881
13	Ca	21.017	9.220	0.996	9.325	9.278
	K	24.930	9.237	0.994	9.323	9.268

Experiment number.

† CXTFIT.

‡ Column holdup.

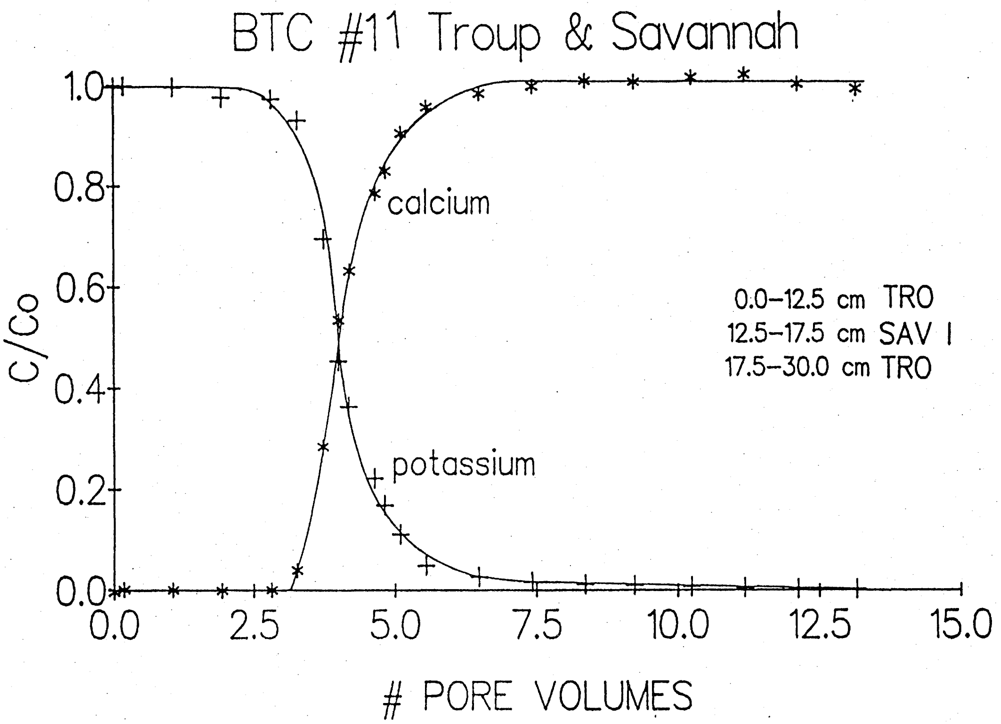


FIG. 11. BTC #11: Ca and K curves for Troup and Savannah soil.

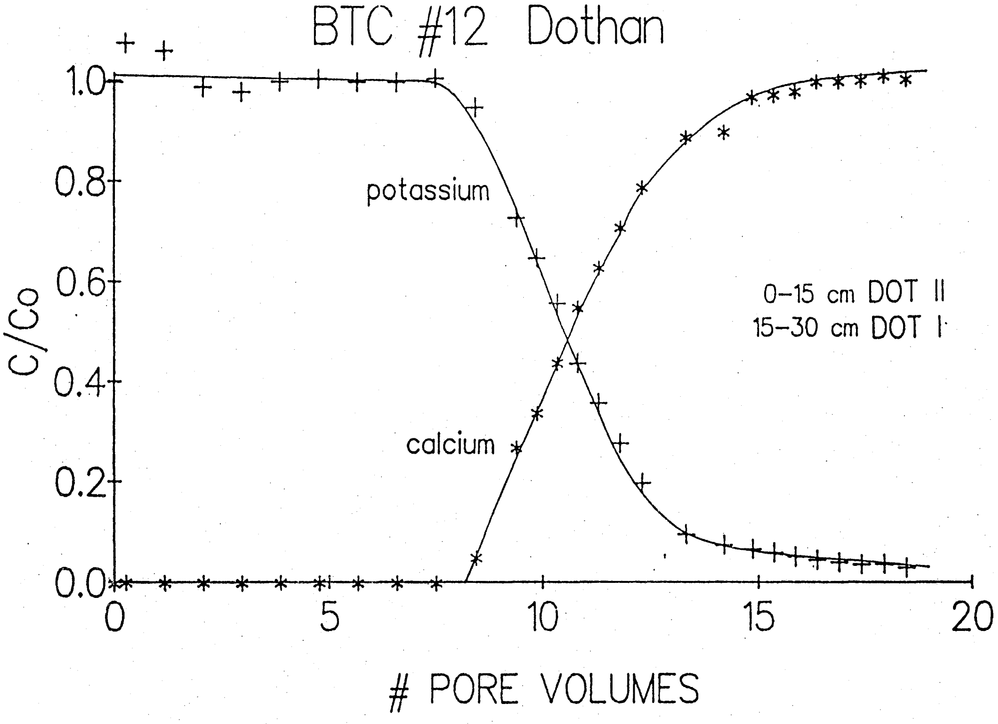


FIG. 12. BTC #12: Ca and K curves for Dothan soil.

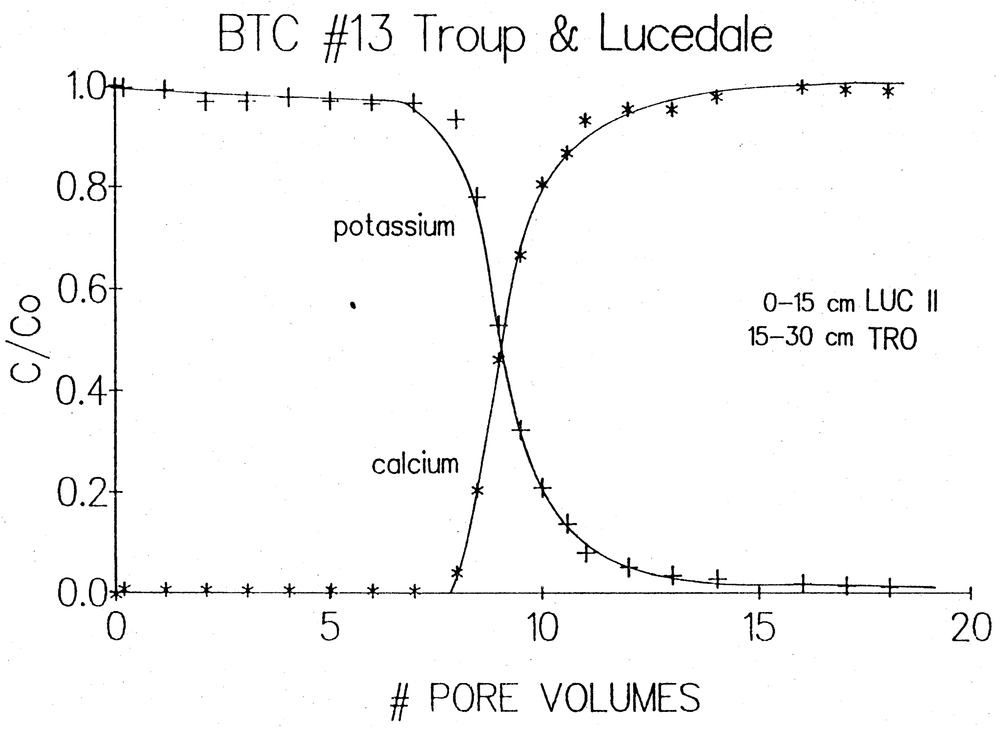


FIG. 13. BTC #13: Ca and K curves for Troup and Lucedale soil.

The results suggest that the BTC for a layered medium might also be obtained with an equivalent, uniform medium. The layering does not seem to have a particular effect on the effluent concentration. This was already concluded (i.e., page 20 and 21) based on the results of Appendix C, which contain expressions for regular, absolute, and central moments for the cases listed in table 1. Therefore, no further investigations of transport in layered media, e.g., an increase in the number of layers, numerical predictions of the BTC, pulse studies, were initiated.

Transport in Homogeneous Media with Binary Exchange

Simultaneous cation and anion displacement experiments were carried out to investigate the effect of possible changes in CEC during transport and to investigate the influence of non-linear exchange on transport. These investigations were accomplished by temporarily replacing the 0.005 *M* $CaBr_2$ eluent (resident) solution with a 0.01 *M* NaCl eluent (pulse) during continuous leaching.

The experimental conditions for the binary exchange study are listed in table 10. Values for θ and v are given as average values because they vary along the column and over time, respectively. T_o denotes the number of pore volumes at which the input line was switched back to the original solution. Its value was obtained from the gravimetrically determined effluent volumes. The BTC's are shown in figures 14 through 21, the symbols denote experimentally determined points and the solid lines are fitted by eye. From these curves it appears that more spreading takes place for the cations than for the

Table 10. Experimental Conditions for Pulse Displacement with Binary Exchange

Experiment #	Soil	ρ_b	ε	$\bar{\theta}$	$\bar{v}$	PV	t_o	T_o	L
		$g\ cm^{-3}$			$cm\ d^{-1}$	cm^3	d		cm
21	Dothan I	1.15	0.57	0.55	100.2	167.1	0.208	1.416	14.8
22	Dothan II	1.23	0.54	0.48	100.0	151.3	0.208	1.376	15.5
23	Wickham I	1.21	0.54	0.43	128.1	132.3	0.208	1.760	15.1
24	Wickham II	1.29	0.51	0.41	116.5	128.4	0.208	1.584	15.3
25	Troup	1.67	0.37	0.31	146.0	93.0	0.347	3.414	14.8
26	Lucedale I	1.32	0.54	0.49	74.1	154.0	0.347	1.165	15.5
27	Lucedale II	1.26	0.52	0.51	91.5	156.2	0.347	2.080	15.1
28	Savannah I	1.42	0.47	0.42	118.8	130.1	0.347	2.595	15.3

Resident solution: 0.005 *M* $CaBr_2$.
Pulse solution : 0.01 *M* NaCl.
I : <250 μm.
II : 500-840 μm.

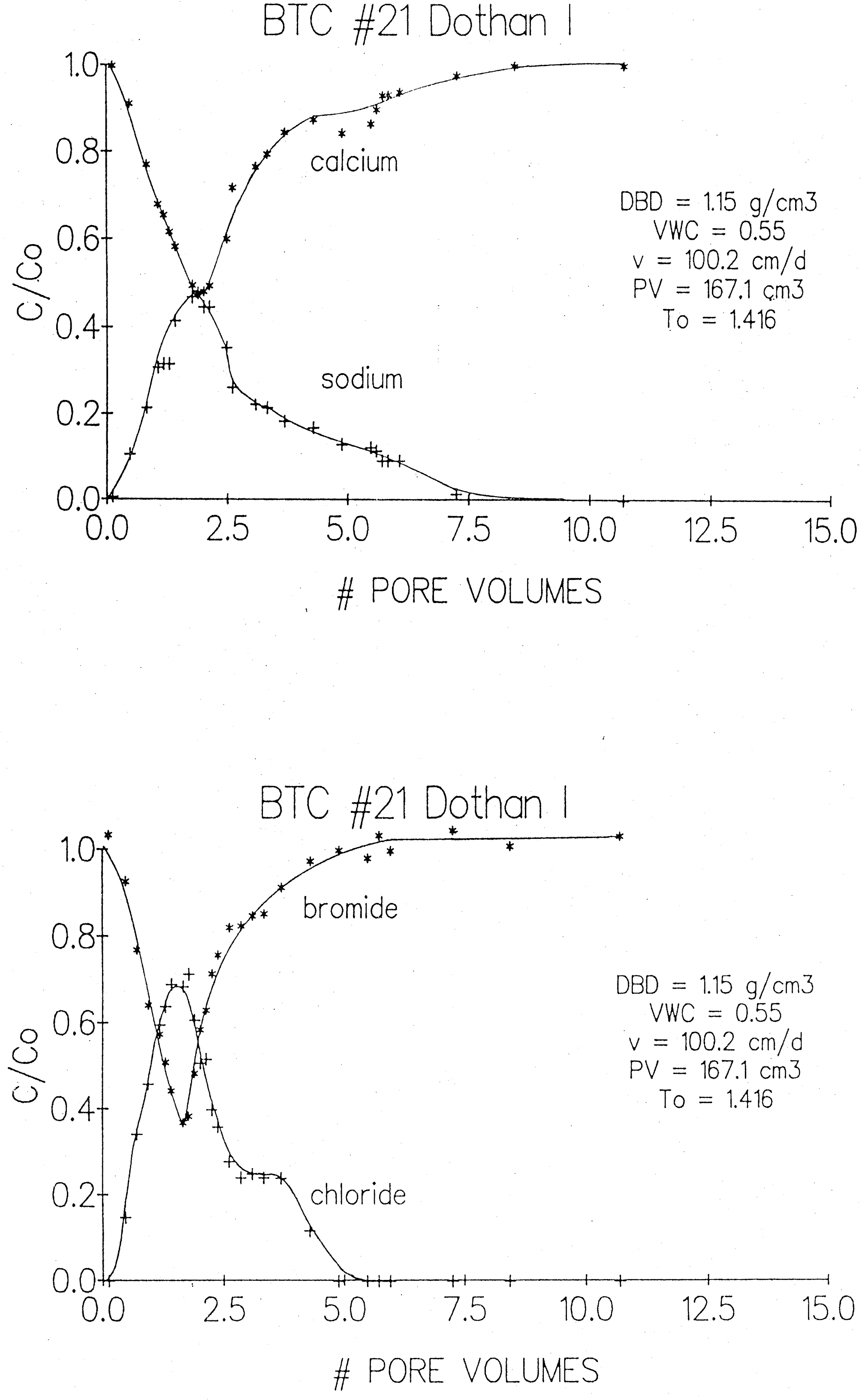
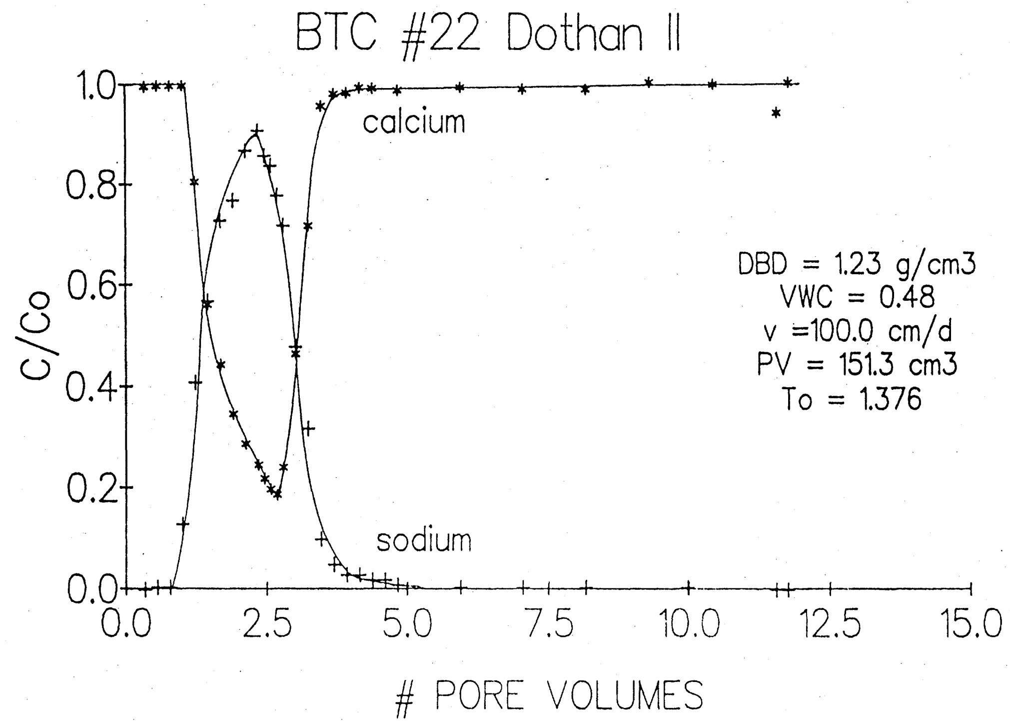


FIG. 14. BTC #21: Ca, Na, Br, and Cl curves for Dothan I.



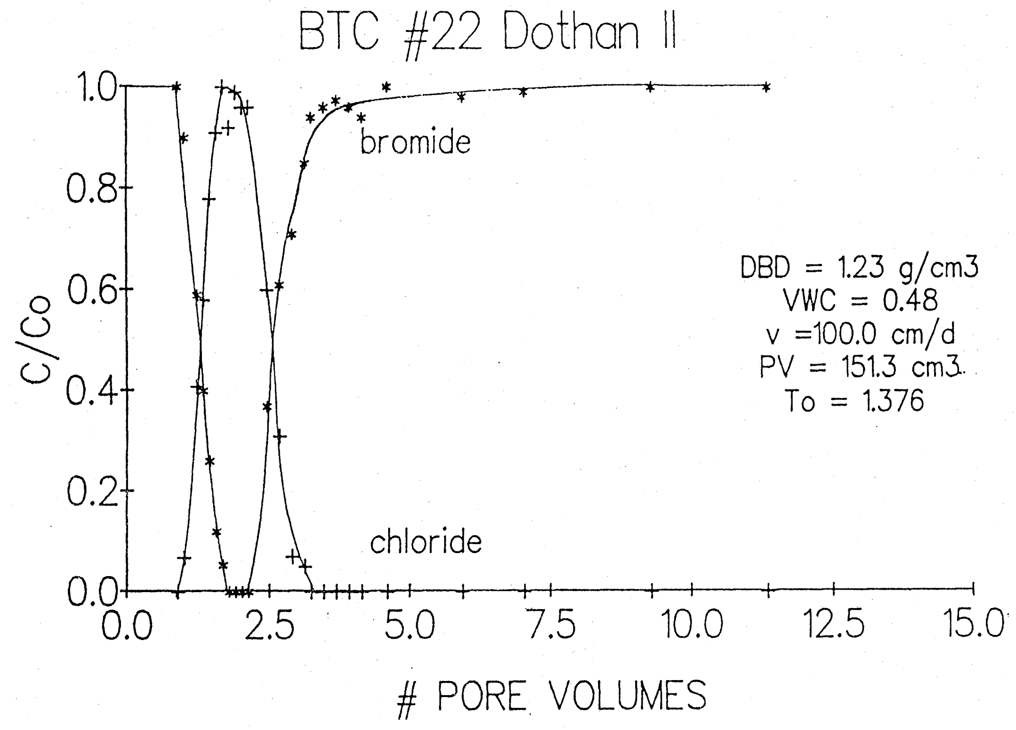
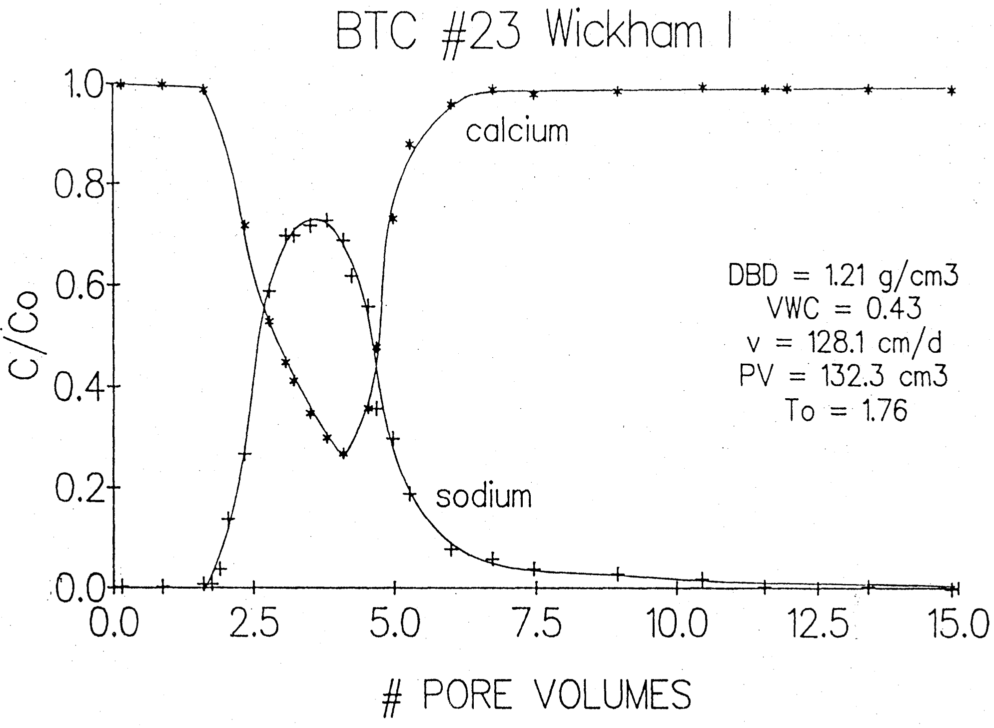


FIG. 15. BTC #22: Ca, Na, Br, and Cl curves for Dothan II.



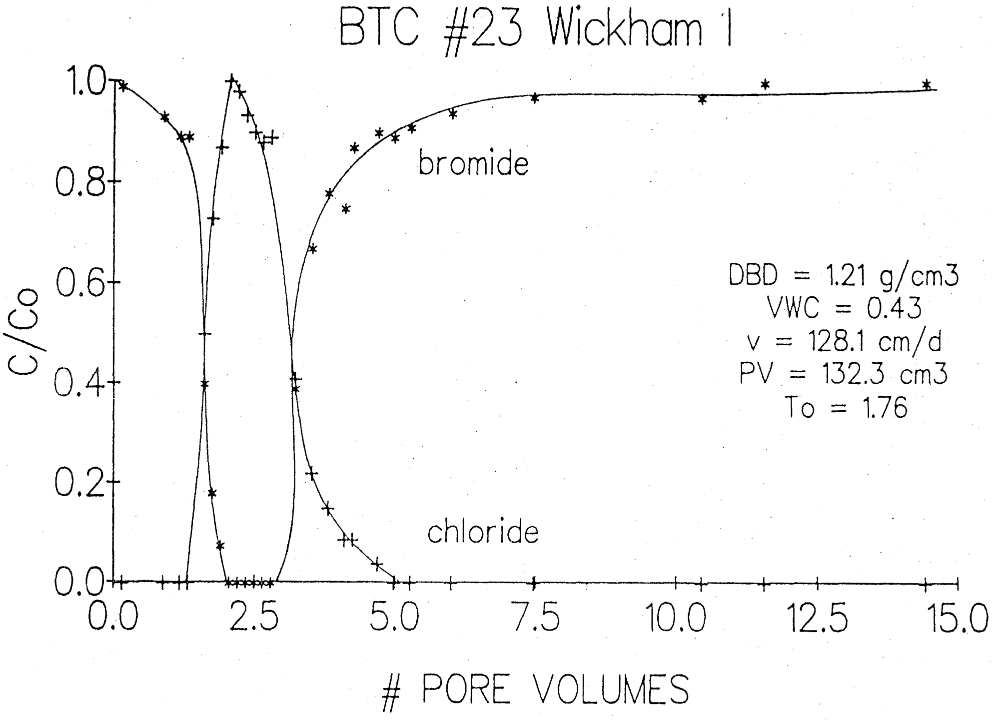
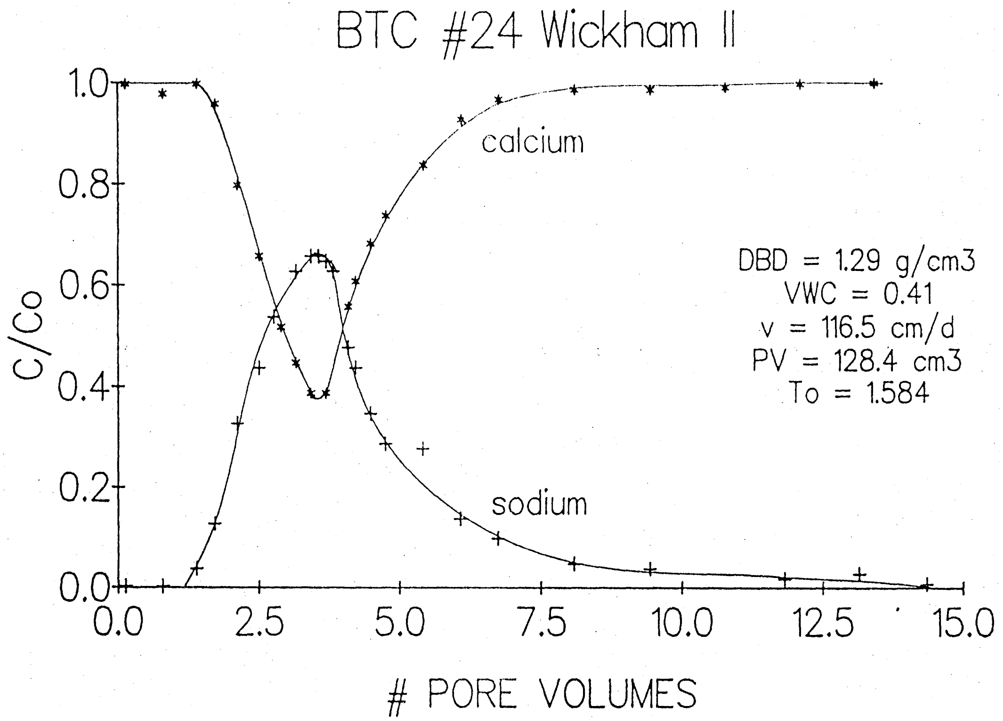


FIG. 16. BTC #23: Ca, Na, Br, and Cl curves for Wickham I.



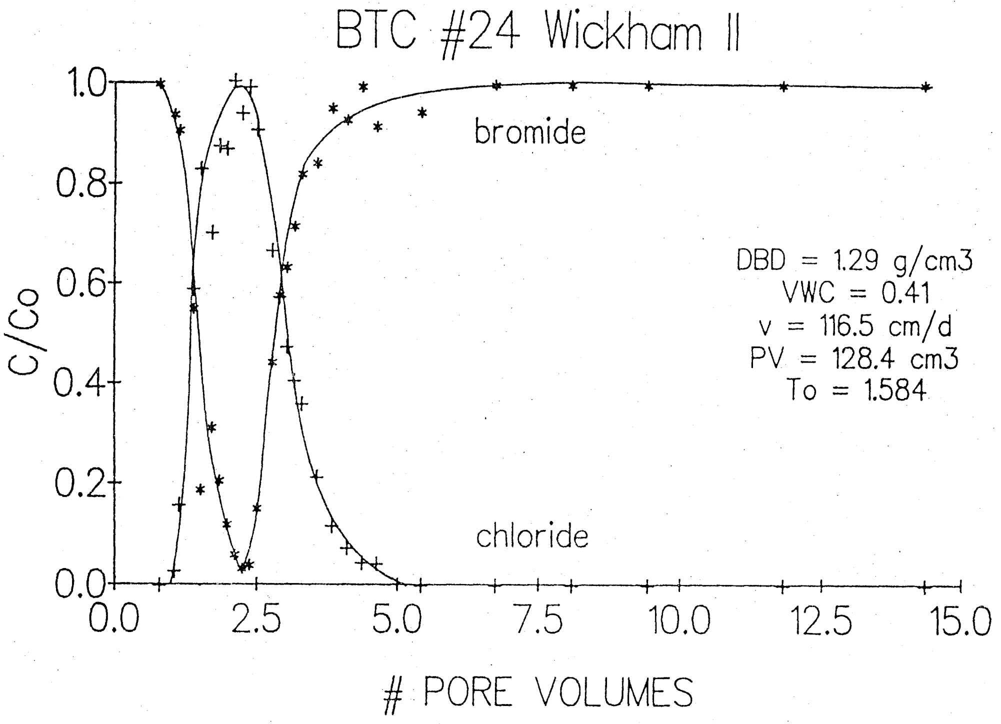
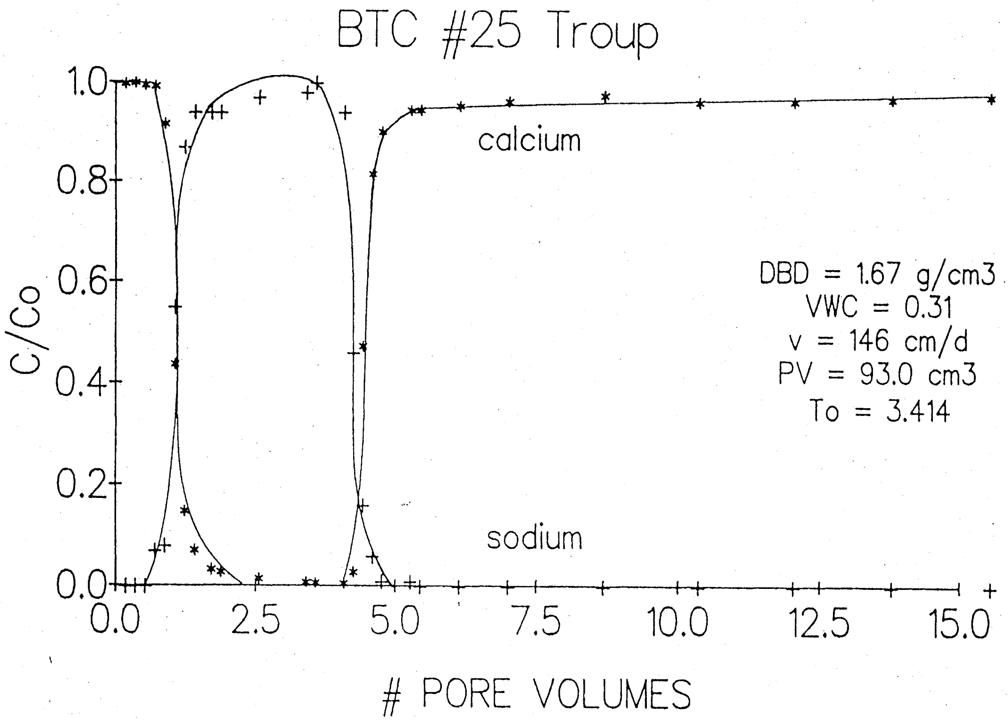


FIG. 17. BTC #24: Ca, Na, Br, and Cl curves for Wickham II.



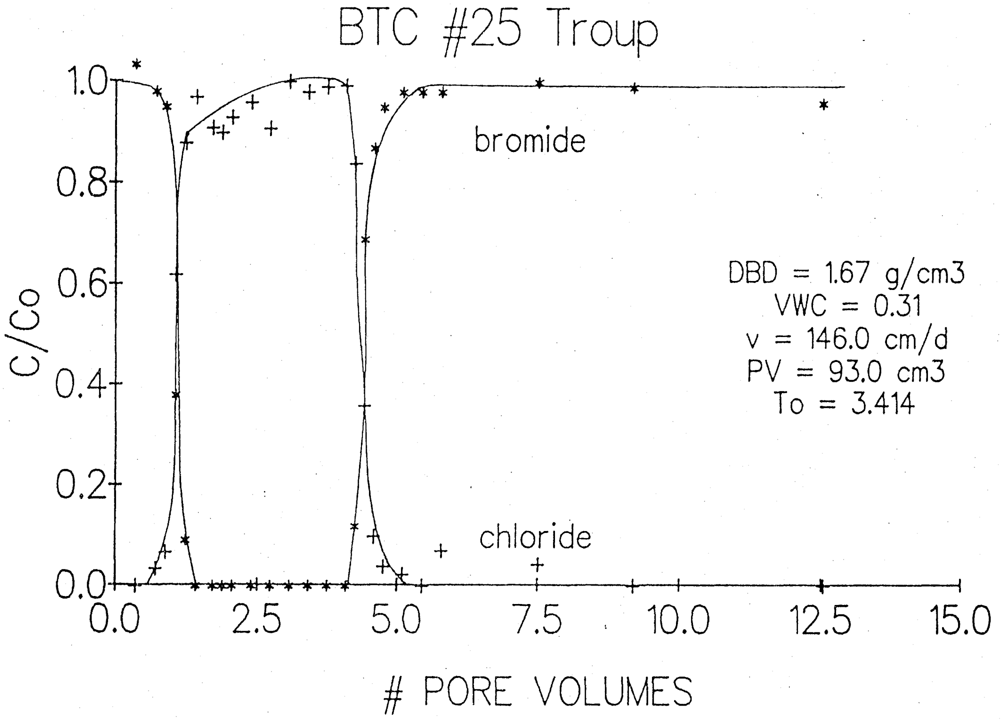


FIG. 18. BTC #25: Ca, Na, Br, and Cl curves for Troup soil.

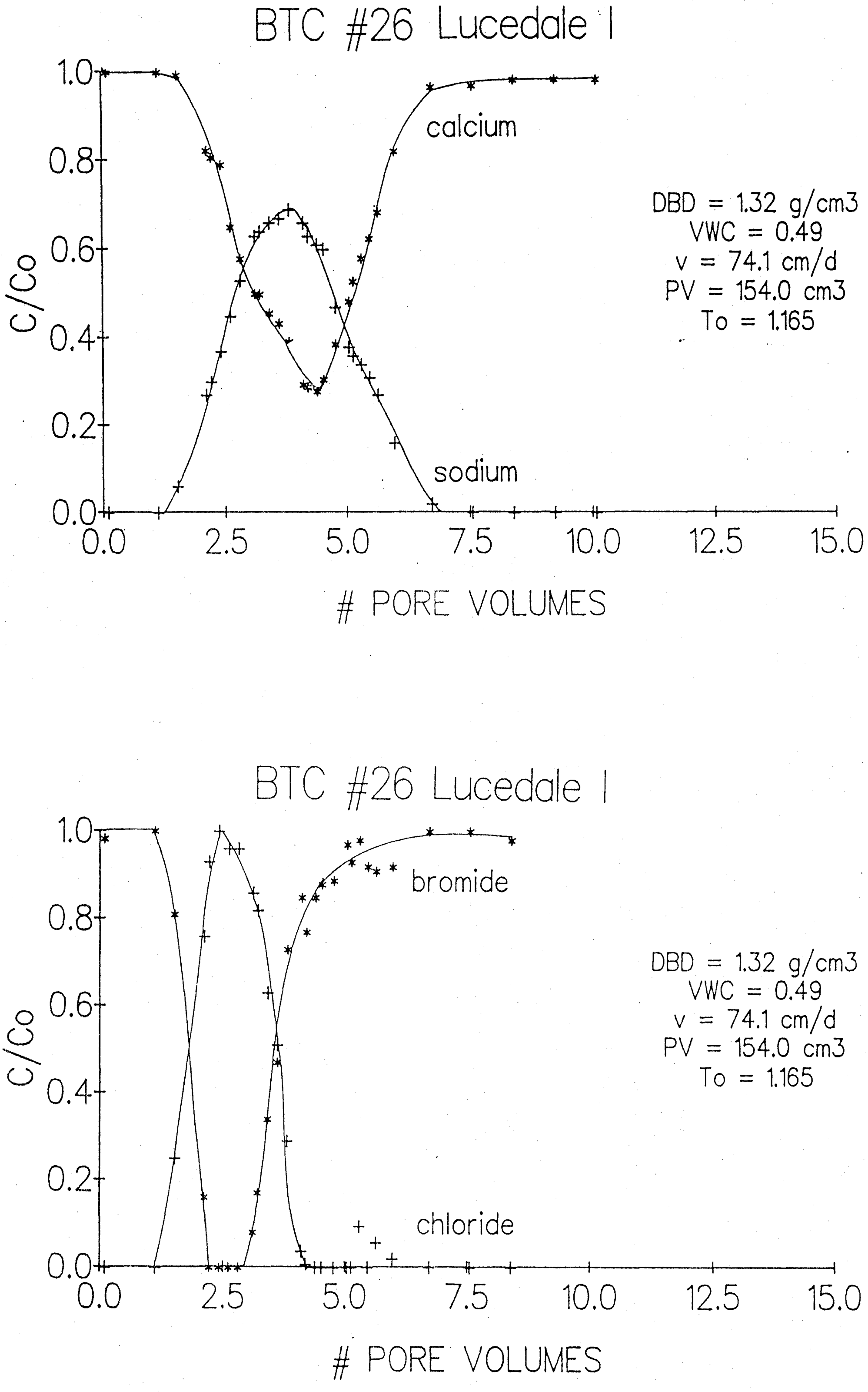
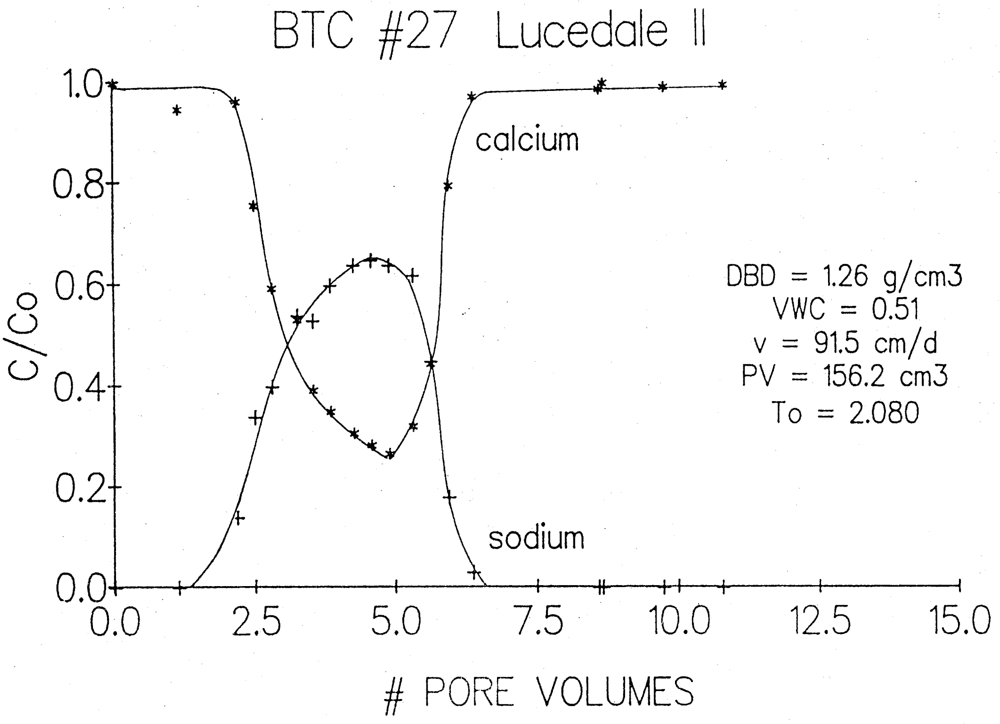


FIG. 19. BTC #26: Ca, Na, Br, and Cl curves for Lucedale I.



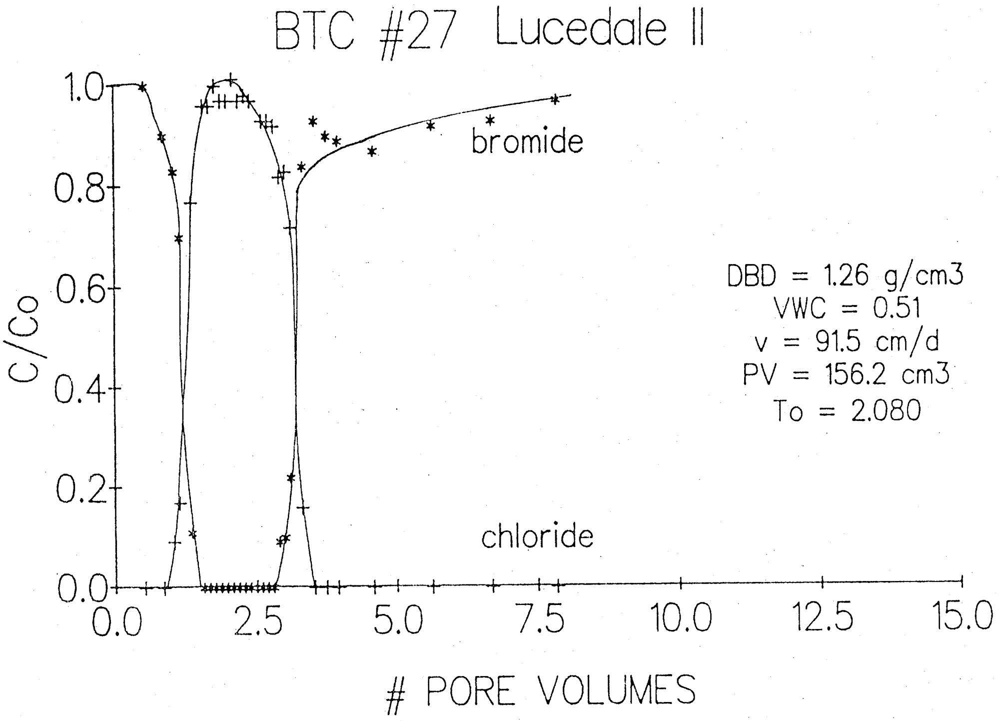
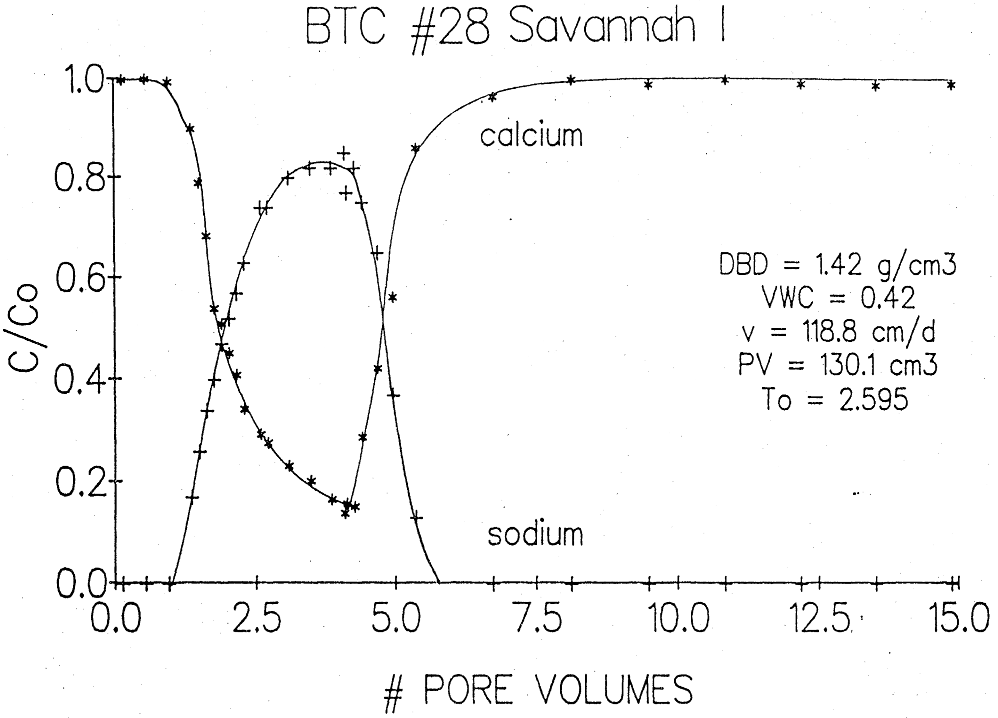


FIG. 20. BTC #27: Ca, Na, Br, and Cl curves for Lucedale II.



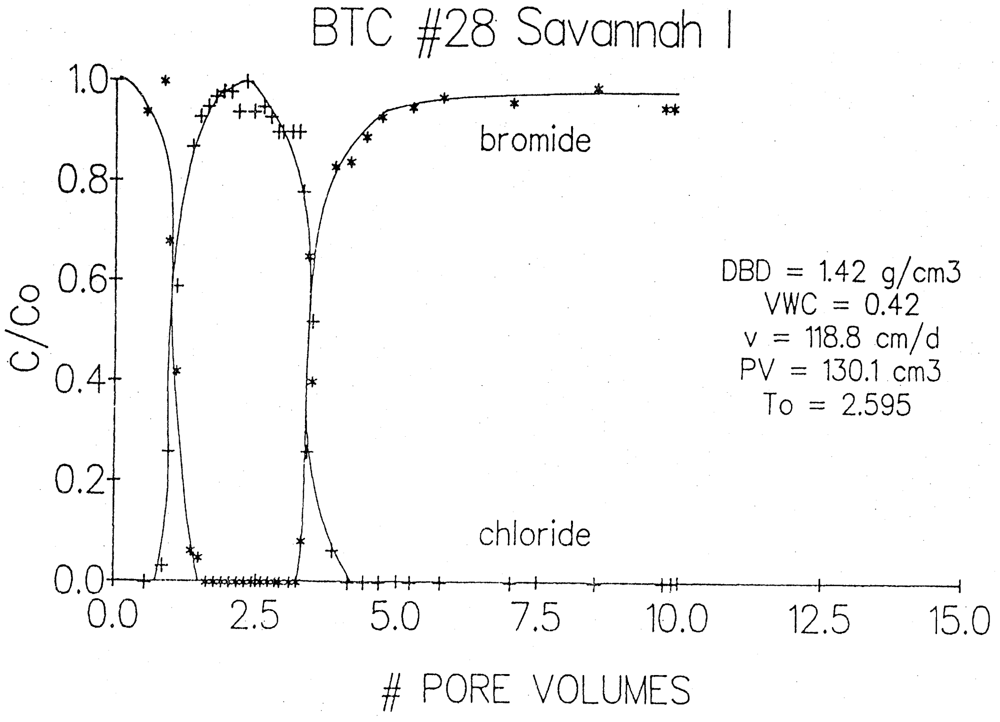


FIG. 21. BTC #28: Ca, Na, Br, and Cl curves for Savannah I.

anions. The peak values of C/C_o are higher for the anions than for the cations. Both cations and anions were retarded, except for the displacement in the Troup soil (figure 18). However, the anions were retarded to a lesser extent than the cations. In a number of cases tailing was observed (e.g., figures 14 and 17).

For further analysis, the $C(T)/C_o$ relationship was used for Na and Cl and the $1-C(T)/C_o$ relationship for Ca and Br. Values for D and R were obtained with the program CXTFIT for a flux-averaged concentration assuming equilibrium conditions. The results are listed in table 11. Although the values for r^2 are smaller than for the experiments involving layered media, they still show a good correlation between experimentally determined and fitted curves. The "inverse" Ca pulse generally exhibits somewhat more retardation than the Na pulse, presumably because more Ca than Na is sorbed by the soil. The differences in R values (table 11) for the anions are rather small, with the exception of experiment 21 where non-equilibrium conditions seemed to exist. The larger values of D for the cations than the anions (except experiment 21) confirm the impression that more spreading occurred for the cations.

It should be noted that for binary systems with constant solute concentrations in the liquid and the adsorbed phases, the concentrations of pulse and resident solutions complement each other. Theoretically, the values for D and R obtained from the displacing and resident solute concentration curves (anions or cations) should, therefore, be equal. This is not always the case, because of non-equilibrium conditions and changes in apparent exchange capacity.

Table 11. Determination of Transport Parameters with Binary Exchange Using CXTFIT

Experiment #	Solute	D	R	r^2	AEC
		cm^2d^{-1}			mol_c/kg
21	Ca	781.56	2.596	0.968	
	Na	518.43	1.914	0.898	
	Br	1326.5	2.343	0.943	0.642
	Cl	543.75	1.459	0.927	0.220
22	Ca	64.48	1.708	0.967	
	Na	60.05	1.587	0.964	
	Br	39.72	1.285	0.977	0.111
	Cl	29.68	1.245	0.983	0.096
23	Ca	71.32	3.041	0.967	
	Na	70.48	2.881	0.985	
	Br	21.37	1.590	0.973	0.210
	Cl	32.61	1.585	0.962	0.208
24	Ca	120.08	3.013	0.988	
	Na	102.65	2.884	0.952	
	Br	93.42	1.389	0.981	0.124
	Cl	87.31	1.487	0.982	0.155
25	Ca	23.53	1.055	0.994	
	Na	48.46	0.963	0.952	
	Br	17.60	1.008	0.991	0.001
	Cl	20.26	1.011	0.948	0.002
26	Ca	58.41	2.804	0.964	
	Na	77.51	2.525	0.972	
	Br	36.18	1.406	0.964	0.151
	Cl	32.22	1.364	0.977	0.135
27	Ca	50.65	3.474	0.918	
	Na	75.91	3.425	0.914	
	Br	6.19	1.173	0.983	0.070
	Cl	13.06	1.196	0.962	0.079
28	Ca	124.69	2.229	0.943	
	Na	128.11	2.227	0.948	
	Br	91.73	1.003	0.953	0.001
	Cl	87.38	0.9942	0.937	-0.002

Second, the moment method was used to analyze the BTC's and determine values for D and R (table 12). Moments up to order three were determined via numerical integration of the BTC according to Eq.(21). The necessary integrations were performed with the trapezoidal rule

Table 12. Determination of Transport Parameters with Binary Exchange Using Time Moments

#	Solute	M_0	M_1	M_2	M_3	μ'_1	μ_2	R	D	PE†
						d	d^2		cm^2d^{-1}	%
21	Ca	1.420	3.956	14.573	65.245	0.411	0.0546	2.078	401.4	0.28
	Na	1.416	4.095	15.702	72.694	0.427	0.0595	2.184	398.3	-
	Br	1.338	3.451	14.086	83.286	0.381	0.0845	1.871	785.4	5.51
	Cl	1.496	3.073	7.807	23.052	0.303	0.0218	1.346	341.3	5.65
RMD‡		2.72	1.64	9.87	21.60				ENE§	=0.04%
22	Ca	1.373	3.463	10.565	43.084	0.390	0.0319	1.834	271.4	0.22
	Na	1.595	3.692	9.634	29.433	0.358	0.0163	1.627	154.7	15.92
	Br	1.430	3.190	8.743	32.169	0.345	0.0272	1.543	319.7	3.92
	Cl	1.249	2.412	4.895	10.389	0.299	0.00454	1.243	19.51	9.23
RMD[%]		0.73	4.30	14.24	30.79					ENE=5.12%
23	Ca	1.830	7.436	37.225	256.06	0.479	0.0532	3.183	340.7	3.98
	Na	1.983	8.202	38.691	213.07	0.487	0.0334	3.256	195.6	12.67
	Br	2.090	6.627	27.514	155.57	0.374	0.0432	2.291	525.1	18.75
	Cl	1.604	4.042	10.883	30.884	0.297	0.00603	1.640	62.8	8.86
RMD[%]		4.44	6.91	13.32	25.58					ENE=1.59%
24	Ca	1.640	6.602	30.983	172.91	0.528	0.0462	3.234	210.4	3.54
	Na	1.584	6.587	31.945	179.33	0.545	0.0494	3.366	208.9	-
	Br	1.593	3.900	10.886	35.057	0.321	0.0143	1.656	201.5	0.57
	Cl	1.735	4.117	10.674	30.090	0.311	0.00896	1.581	110.7	9.53
RMD[%]		1.31	0.95	0.89	0.35					ENE=1.59%
25	Ca	3.825	14.531	95.293	763.61	0.385	0.1077	2.093	2344	12.13
	Na	3.319	9.204	29.064	100.27	0.281	0.0110	1.068	89.0	2.70
	Br	3.387	9.372	29.572	103.59	0.280	0.0110	1.062	90.0	0.70
	Cl	3.391	9.869	34.218	138.76	0.295	0.0166	1.205	475.4	0.59
RMD[%]		3.61	10.46	32.73	56.78					ENE=5.26%
26	Ca	1.820	6.651	26.920	121.42	0.745	0.0598	2.822	82.0	9.31
	Na	1.801	5.924	21.180	81.185	0.671	0.0391	2.457	63.2	8.17
	Br	1.534	3.734	9.817	27.707	0.497	0.0197	1.602	49.4	7.88
	Cl	1.469	3.278	7.678	18.767	0.455	0.0103	1.399	1.78	11.77
RMD[%]		1.27	6.04	12.01	19.74					ENE=9.33%
27	Ca	2.201	9.439	43.470	211.90	0.708	0.0370	3.249	64.8	5.82
	Na	2.077	8.696	38.775	181.95	0.691	0.0310	3.147	53.7	0.14
	Br	2.268	5.704	17.221	63.429	0.567	0.0345	1.475	285.3	9.04
	Cl	1.909	4.231	10.009	24.993	0.575	0.0090	1.176	-41.0	8.22
RMD[%]		5.71	7.89	10.88	14.18					ENE=1.19%

Continued

Table 12. Determination of Transport Parameters with Binary Exchange Using Time Moments

#	Solute	M_0	M_1	M_2	M_3	μ'_1	μ_2	R	D	PE
						d	d^2		$cm^2 d^{-1}$	%
28	Ca	2.611	8.939	36.662	192.45	0.440	0.0384	2.126	343.9	0.62
	Na	2.524	8.082	28.449	107.33	0.412	0.0168	1.905	102.2	2.74
	Br	2.499	5.888	15.411	43.896	0.303	0.0102	1.059	8.1	3.70
	Cl	2.338	5.295	13.178	35.240	0.291	0.0084	0.967	-92.6	9.90
RMD[%]		2.49	5.14	11.15	24.75				ENE=2.99%	

† $\left[|C_oT_o-M_0|/C_oT_o\right]\times100\%$.

‡ $(0.5/\bar{M})\left[|0.5(M_{Ca}+M_{Br})-\bar{M}| + |0.5(M_{Na}+M_{Cl})-\bar{M}|\right]\times100\%$ and

$\bar{M} = 0.25(M_{Ca}+M_{Br}+M_{Na}+M_{Cl})$.

§ $\left[|(\overline{M_0})_{cat} - \overline{M_0}|/\overline{M_0}\right]\times100\%$.

because the increments in T were not constant. The results (table 12) include the values of several measures to evaluate the accuracy of the experimentally determined BTC's. These measures, indicated as PE, RMD and ENE, will be discussed first, after which attention will be focused on the determination of D and R.

For each solute, a measure of the difference between the amount of solute in the applied eluent pulse (C_oT_o) and in the observed effluent pulse (M_0) was calculated. This measure, the pulse error PE, is an indication of the reliability of the experiments due to errors in analytical and experimental techniques and incomplete displacement. Its value was less than 10% on average, which was considered acceptable.

Differences in values of the various moments of the BTC's for an individual solute pulse ($CaBr_2$ or NaCl) compared to the average of that moment for both pulses are given by the relative mean deviation, RMD. The higher order moments exhibit greater differences, presumably because of the inability to accurately determine the tail of the BTC, resulting in larger values for RMD. The contribution of the tail to the higher moments is relatively large. Errors in parameter estimation as a result of experimental errors in the tailing portion of the BTC are a well known disadvantage of the moment method although some modifications can be made to overcome this problem *(25)*.

The electroneutrality principle was evaluated by the relative error, ENE, which was defined based on the difference between the average mass of the cation pulse, $(M_{0,Ca}+M_{0,Na})/2$, and the average mass of the total solute pulse $(\bar{M}_0)$, $(M_{0,Ca}+M_{0,Na}+M_{0,Cl}+M_{0,Br})/4$, for the effluent. This relative error, ENE, is generally smaller than PE, because it is averaged over two ionic pulses and does not account for differences between the eluent and effluent pulse.

The sums of cations and anions were determined for the various BTC's to investigate the hypothesis that the effective CEC is higher for a Ca medium than for a Na medium. In such an event, the Na pulse would decrease the cation equivalents in the adsorbed phase and, therefore, temporarily increase the cation equivalents in the liquid phase. Because of the electroneutrality principle, the anion equivalents in the liquid phase should change correspondingly. Although a slight increase in the total amount of cations in the effluent was observed in some instances during the occurrence of the Na peak, the low values for PE and ENE did not warrant the conclusion that the CEC had changed. Such changes might not have happened anyhow, because the pulse type displacement is of relatively short duration and the soil is not saturated with the cation applied in the pulse. The BTC's, and previously measured exchange curves *(12)*, indicate that the majority of adsorption sites in a Na/Ca system are always occupied by Ca during these experiments, whereas changes in CEC presumably take place only when highly favorably adsorbed Ca ions are actually displaced. Further investigations are needed to pursue this issue, preferably by determining solute concentrations in the adsorbed and liquid phase as a function of distance rather than a function of time at the outlet.

Using moments allowed us to evaluate BTC's and calculate values for D and R. First values for R in the binary systems (table 12) were obtained according to Eq.(22). Second, values for μ_1' (mean breakthrough time) and μ_2 (average pulse spread) were determined according to Eq.(18) and (24), respectively, where we used T instead of t (Eq.(9)). These variables are useful to characterize the BTC. Third, the value of the dispersion coefficient was determined by relating D and μ_2. Upon substitution of v^* and D^* for v and D in the expression for μ_2 in Appendix C, the following theoretical expression was obtained:

$$\mu_2(L) = \frac{t_o^2}{12} + 2\,\frac{LDR^2}{v^3} \qquad (28)$$

where the "first-type" expression was used because the values of the concentration are flux-averaged. This equation was solved for D, the results of which are also included in table 12. The values for D vary widely and include even some negative values. They do not seem very reliable based on the BTC's shown in figures 14 to 21. This was attributed to the small values of the experimentally determined $\mu_2(L)$ as a result of the small amounts of solute spreading that occurred in the soil columns. The part of the expression for μ_2 which is independent of position, the inlet effect, $t_o^2/12$, dominates and no accurate prediction for D can therefore be made.

It should be noted that the more common approach is to obtain BTC's at two positions, x_1 and x_2 *(10)*. D is then determined according to Eq.(26-b), which is the proper way to determine dispersion inside the porous medium, particularly if boundary effects contribute significantly to solute spreading (as in, e.g., short laboratory columns).

Finally, an attempt was made to numerically predict the BTC's for cation displacement using experimentally determined exchange isotherms *(12)* and values for D determined from the simultaneous anion displacement experiments using CXTFIT (table 11). Because the dependency of the CEC value on the Ca and Na concentration was not known, the CEC was assumed to be constant. Its value was determined from the average R value for Ca and Na, presented in table 12, and ρ_b and θ, listed in table 10. Use of an average R value resulted in one effective value for the CEC, i.e., the exchange was assumed to be linear *(20)* over the observed jump in solute concentration. Eq.(2) and (3) were solved numerically with a Crank-Nicolson scheme for a third-type condition. Values for $\partial S/\partial C$ were obtained from Appendix E.

The predicted curves, along with the measured solute concentrations, are shown in figure 22. The curves match the observed

BTC's with varying degrees of success. The average position of the pulse is generally predicted fairly adequate as is the shape of the pulse; Ca desorption is accompanied by spreading and Ca adsorption accompanied by steepening of the front. In some instances, numerical oscillations were encountered because of large variations in D^* and v^*, depending on the solute concentration in the liquid phase. Furthermore, for some of the isotherms, $\partial S/\partial C$ changed sign during passage of the front. A scheme with a variable time step might have improved the results. Also, some of the exchange isotherms were probably not highly accurate, resulting in poor predictions of $\partial S/\partial C$, and hence R according to Eq.(3). However, most of the exchange isotherms seem to characterize the exchange process reasonably well and could succesfully be used to predict the BTC's numerically.

Values for the anion exchange capacity, AEC, were obtained by using an average R value for Cl and Br from table 11 and values for ρ_b and θ from table 10, i.e., similarly as for the CEC. It appears that anion adsorption can generally not be ignored for these soil types. Since values for the AEC are strongly dependent on pH, it should be noted that the pH values of the effluent were generally close to that of the 0.005 M $CaBr_2$ resident solution.

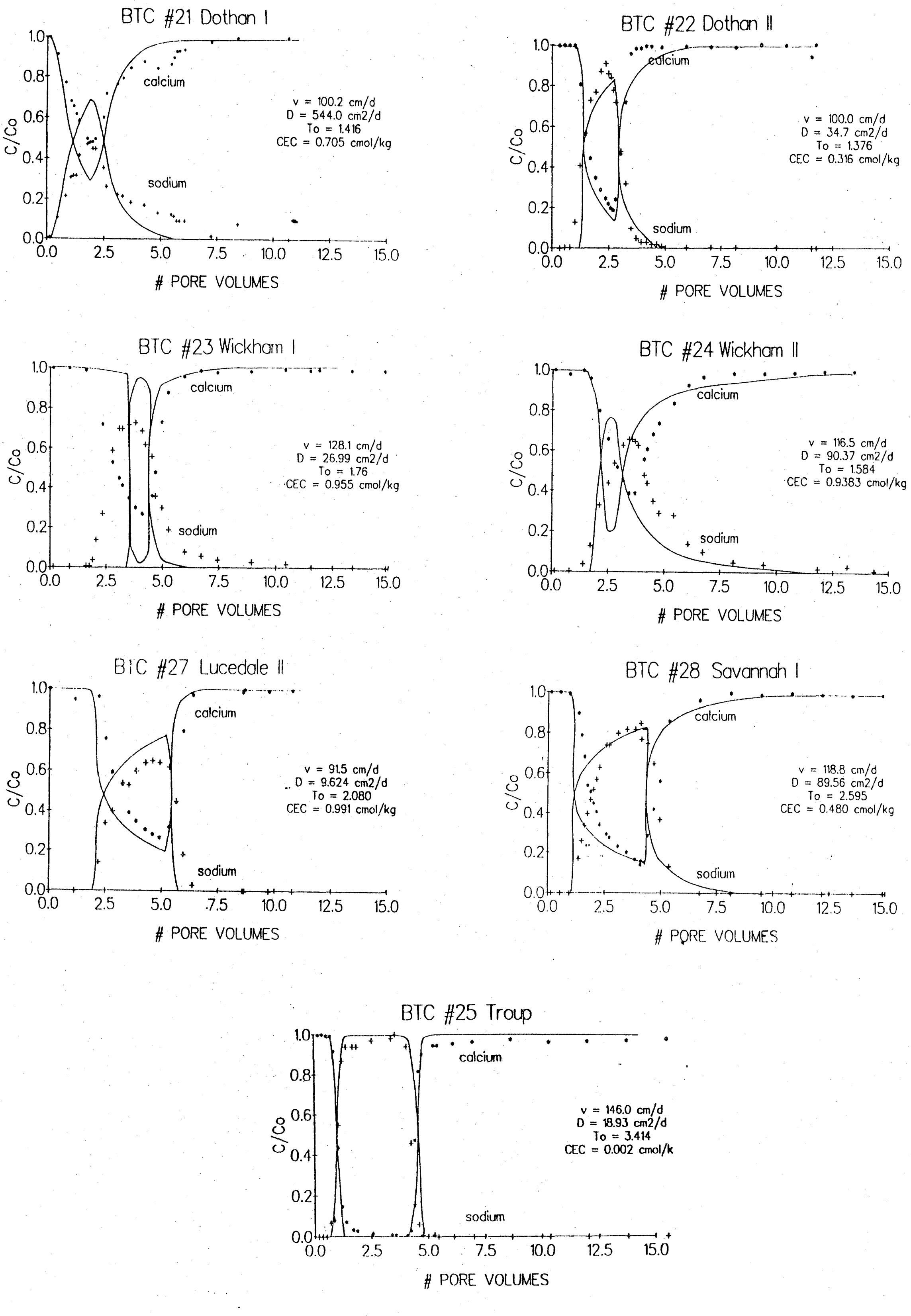


FIG. 22. Numerically predicted (solid lines) and experimentally determined curves (symbols) for cation displacement in binary systems.

Transport in Homogeneous Media with Ternary Exchange

To further investigate the effect of non-linear cation exchange, BTC's were determined using three different cations. A pulse containing a favorably (K) and an unfavorably (Na) exchanging solute was applied to soils containing Ca as the resident cation. The experimental conditions for these displacement studies are listed in table 13; the same soil columns as for experiments 21-24 were used.

Table 13. Experimental Conditions for Solute Displacement with Ternary Exchange

Experiment #	Soil	ρ_b	ε	$\bar{\theta}$	$\bar{v}$	PV	t_o	T_o	L
		g cm^{-3}			cm d^{-1}	cm^3	d		cm
31	Dothan I	1.15	0.57	0.55	99.24	167.1	0.434	2.838	14.8
32	Dothan II	1.23	0.53	0.48	98.25	151.3	0.434	2.699	15.4
33	Wickham I	1.36	0.49	0.47	98.55	145.8	0.306	1.999	15.1
34	Wickham II	1.29	0.51	0.45	120.0	138.4	0.306	2.392	15.3

Resident solution: 0.005 *M* $CaBr_2$.
Pulse solution : 0.005 *M* KBr and 0.005 *M* NaBr.

I : <250 μm.
II : 500-840 μm.

The BTC's for these experiments are shown in figures 23 to 26. For all curves, Na appeared earlier in the effluent than K, because the latter is favorably adsorbed. With the exception of maybe Dothan II (figure 24), considerable tailing seemed to occur for K. Tailing was less pronounced for Na. Based on this, and in light of the anion displacement experiments which showed fairly symmetrical BTC's, we conclude that tailing is primarily due to non-linear exchange and not to physical non-equilibrium. The magnitude and location of the peaks

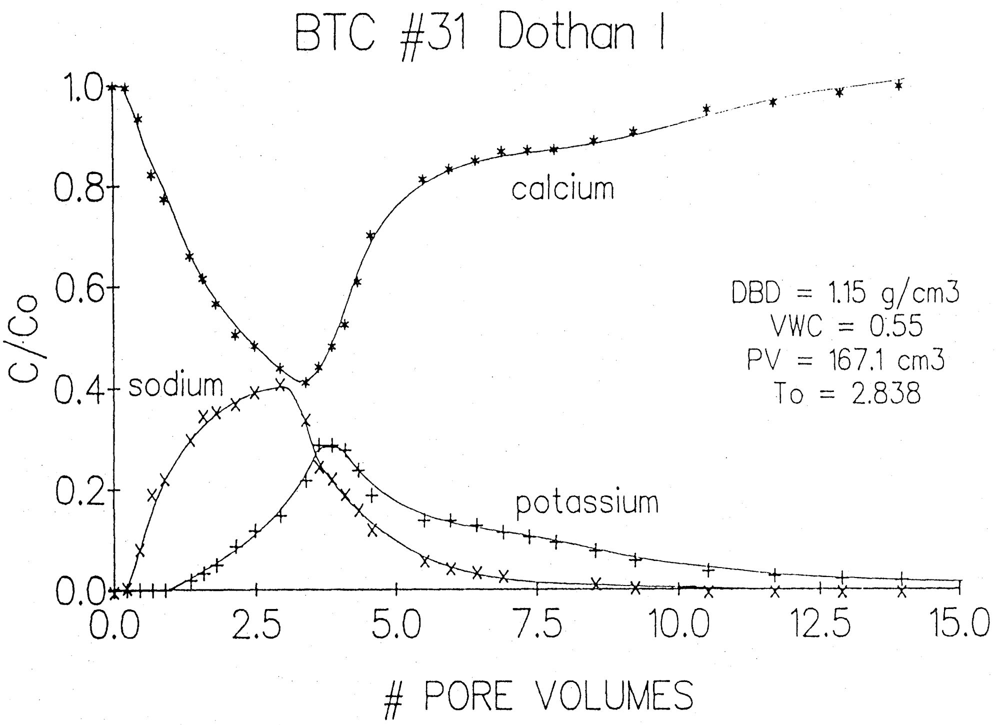


FIG.23. BTC #31: Ca, Na, and K curves for Dothan I.

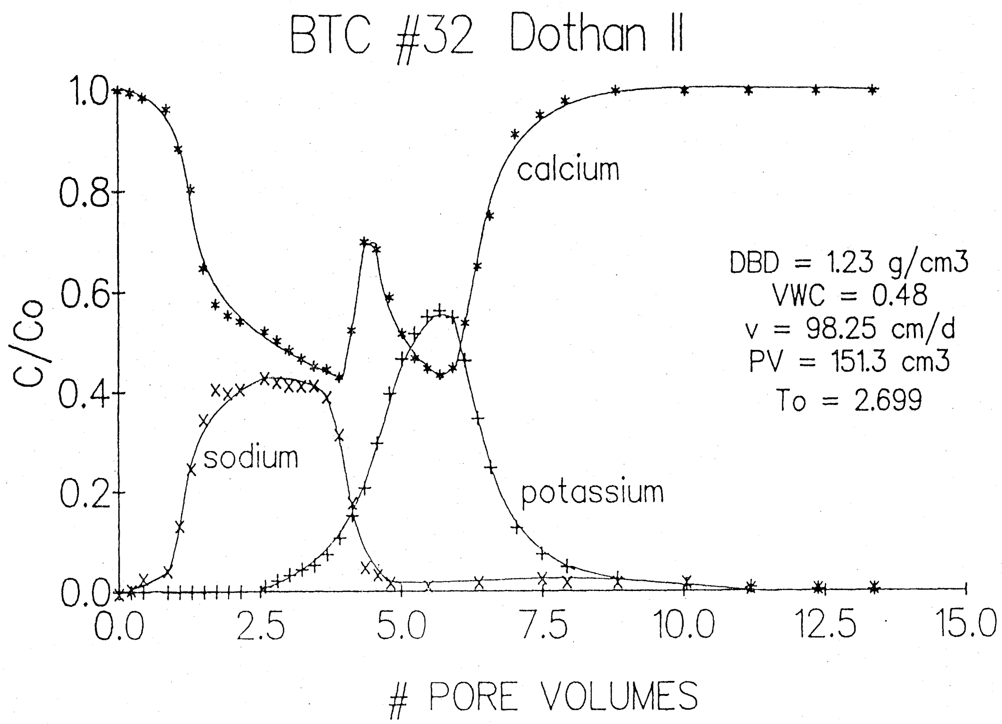


FIG.24. BTC #32: Ca, K, and Na curves for Dothan II.

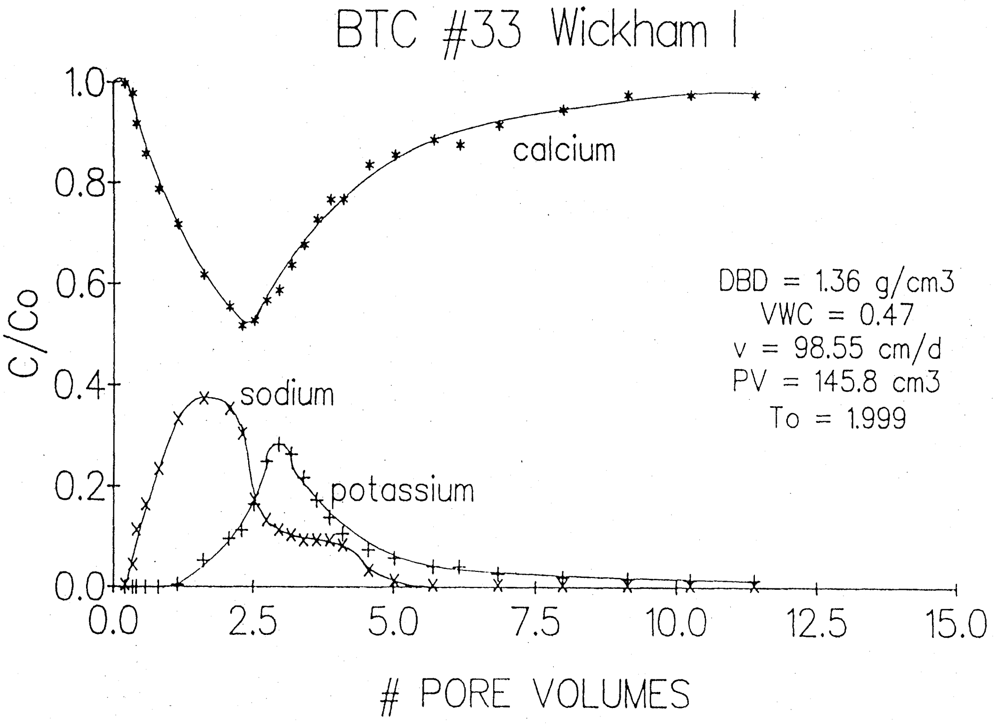


FIG. 25. BTC #33: Ca, K, and Na curves for Wickham I.

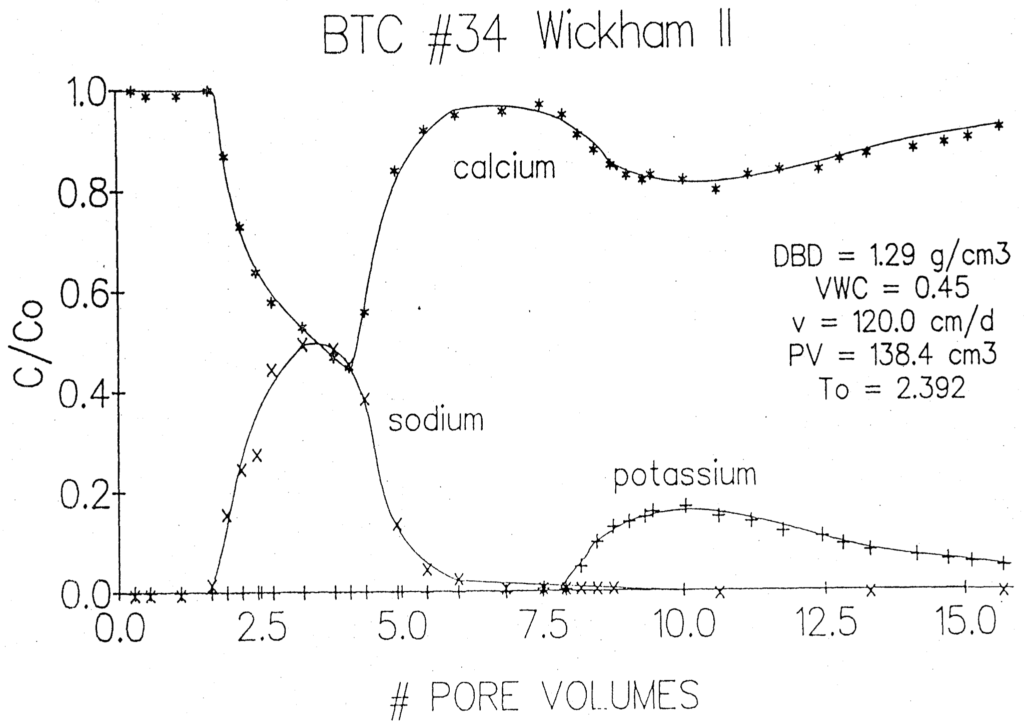


FIG. 26. BTC #34: Ca, K, and K curves for Wickham II.

of the BTC's vary substantially, depending on the exchange process and hydrodynamic dispersion. As for binary exchange, the Ca curve can be viewed as complementary to the BTC for the other cations in the pulse, viz. Na and K. In this ternary system the complementary Ca pulse cannot be used for BTC analysis.

The transport parameters D and R were determined with the program CXTFIT (table 14). The input files are given in Appendix D. In order to use the program, C_o was chosen to be equal to the eluent concentration of the solute, thus, C/C_o varies between 0 and 1. The differences in R for the three cations are substantial. The retardation is largest for K and smallest for Na. Ignoring the results for the complementary Ca pulse, it appears that the values for D vary rather widely from soil to soil. The D values for the binary systems showed considerably less variation. This might be attributed to the effects of non-linear

Table 14. Determination of Transport Parameters with Ternary Exchange Using CXTFIT

Experiment #	Solute	D	R	r^2
		cm^2d^{-1}		
31	Ca	1315.8	3.978	0.973
	K	639.72	5.489	0.902
	Na	840.46	1.642	0.993
32	Ca	481.14	3.602	0.705
	K	24.82	4.323	0.935
	Na	44.79	1.325	0.982
33	Ca	1645.9	4.475	0.980
	K	607.03	4.425	0.811
	Na	1965.7	1.906	0.958
34	Ca	1022.6	5.886	0.577
	K	81.84	11.022	0.836
	Na	42.73	2.286	0.986

exchange, which occurred to a larger extent in the ternary experiments than in the binary experiments (using the same columns).

Next, the moments of the BTC's were determined (table 15), as in the section on binary exchange, to obtain values for D and R and to get an impression of the reliability of the experimental BTC's. The errors PE and RMD appear to be of similar magnitude as for the binary systems (table 12). The relatively large amount of K not recovered in experiments 31 and 33, indicated by the high values of the relative pulse error, PE, was partly caused by incomplete displacement (tailing). The values for R are roughly the same as those obtained with CXTFIT (table 14). However, less outlying values for D were obtained with the moment method than with CXTFIT (cf. #32 and 33).

It should be noted that a general advantage of the method of moments is that the moments can be used to (explicitly) characterize experimental concentration distributions in time or space, independent of any model. Next, they can be used to determine parameters for a certain model. With the curve fitting technique, experimental data are directly fitted to the theoretical solution of a particular model. This does not give as much flexibility to determine transport parameters and provides a less objective basis to characterize the concentration distribution. Some disadvantages of the moment method are that the method is not very accurate if the BTC exhibits substantial tailing and that the BTC needs to be determined at more than one position in the direction of flow for best results.

Table 15. Determination of Transport Parameters with Ternary Exchange Using Time Moments

#	Solute	M_0	M_1	M_2	M_3	μ'_1	μ_2	R	D	PE†
						d	d^2		$cm^2 d^{-1}$	%
31	Ca	2.669	11.449	67.786	506.14	0.640	0.1556	2.871	560.4	5.95
	K	1.236	7.116	50.458	423.35	0.859	0.1707	4.338	272.0	12.90
	Na	1.432	4.240	16.416	78.77	0.442	0.0600	1.542	615.2	0.91
RMD‡		0.02	0.41	0.68	0.40					
32	Ca	2.615	10.554	49.563	257.13	0.633	0.0655	2.686	212.6	3.11
	K	1.360	7.845	48.101	316.95	0.904	0.0514	4.419	56.3	0.78
	Na	1.394	4.631	22.113	150.41	0.521	0.1186	1.973	814.0	3.30
RMD[%]		2.59	8.35	17.24	29.01					
33	Ca	1.577	5.043	21.236	110.04	0.490	0.0761	2.198	448.0	21.11
	K	0.689	2.900	15.564	104.14	0.645	0.1144	3.209	328.1	31.07
	Na	0.940	2.300	9.071	54.54	0.375	0.0860	1.447	1184	5.98
RMD[%]		1.62	1.53	7.41	18.10					
34	Ca	2.202	15.217	143.16	1597.87	0.881	0.2806	5.715	471.7	7.94
	K	0.840	9.404	109.12	1306.00	1.427	0.0743	9.999	37.6	9.77
	Na	1.296	4.669	18.304	78.46	0.459	0.0186	2.407	105.2	8.36
RMD[%]		1.52	3.91	5.82	7.16					

† $\left[|C_oT_o-M_0|/C_oT_o\right]\times 100\%$.

‡ $(0.5/\bar{M})\left[|M_{Ca}-\bar{M}|+|M_{Na}+M_K-\bar{M}|\right] \times 100\%$ and $\bar{M} = 0.5(M_{Ca}+M_K+M_{Na})$.

The utility of D and R values obtained with the moment method was investigated by numerically solving the transport equation and using the values listed in table 15. The resulting BTC's are shown in figure 27, along with curves by using fitted D and R values obtained with CXTFIT. Since we used a constant value for R, the prediction assumes linear exchange. Furthermore, the assumption was made that equilibrium conditions existed and that the solute level in liquid and adsorbed phases was constant. Obviously, this precludes a close fit with experimental data. However, the position of the peak is predicted

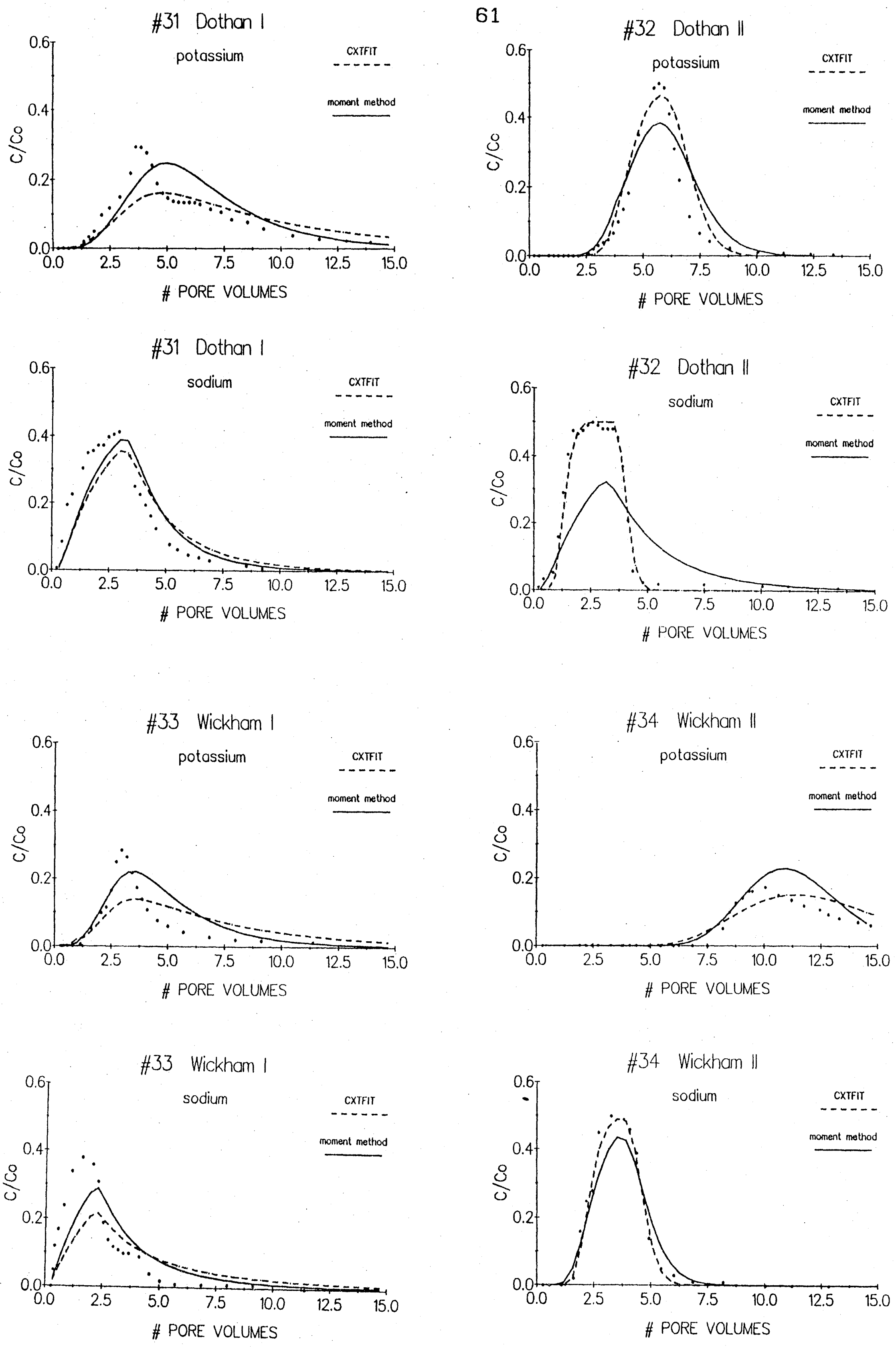


FIG. 27. K and Na curves predicted with the moment method (solid lines) and curve fitting (dashed lines), and experimental curves (symbols) for displacement with ternary exchange.

fairly accurately, along with the time interval for which solute appears in the effluent. Although the curve fitting program is designed to yield D and R values, which produce the "best" fit to the experimental data, a slightly better fit was occasionally obtained with moment generated D and R values (experiments 31 and 33). As stated earlier, the main advantage of the moment method is the quantification of the BTC independent of a particular transport model and its use in theoretical analysis of solute transport. The moment method also seemed more suitable for our ternary system (#31-34), for which the BTC's exhibited considerably more spreading, due to exchange, and the inlet effect was less important, than for the binary system (#21-28). The importance of solute spreading relative to column inlet effects should grow with increasingly longer columns for linearly exchanging and non-reactive solutes, making the moment method more suitable to estimate transport parameters for longer columns.

The effect of non-linear exchange on spreading and tailing during transport with ternary exchange was also investigated using theoretical moments. Values of these moments were calculated in such a way that the effects of non-linear exchange were eliminated as much as possible. Therefore, we used D values obtained from anion displacement experiments in the same soil columns (table 11), adjusted for differences in v between the binary and ternary exchange experiments, and values for R from table 15. The R values and the adjusted D values are listed in table 16, along with the expressions for and the numerical values of the theoretical moments M_1, M_2 and M_3. It was

Table 16. Theoretical Moments Based on Linear Exchange and Their Contribution to Experimental Time Moments for BTC's with Ternary Exchange†

#	Solute	D	R	M_0	M_1	M_2	M_3	μ'_1	NLRT†	μ_2	NLSP§
		cm^2d^{-1}						d	%	d^2	%
31	Ca	544.0	2.871	2.910	15.684	118.33	957.42	0.804	-20.4	0.258	-39.7
	K	544.0	4.338	1.455	10.767	112.25	1629.1	1.104	-22.2	0.497	-65.7
	Na	544.0	1.542	1.455	5.192	35.209	133.98	0.532	-17.0	0.255	-76.5
32	Ca	34.09	2.686	2.769	11.438	49.961	576.49	0.647	2.2	0.025	165.2
	K	34.09	4.419	1.384	8.172	50.401	1479.49	0.926	2.4	0.037	38.2
	Na	34.09	1.973	1.384	4.710	17.162	219.28	0.533	-2.3	0.021	475.7
33	Ca	20.8	2.198	1.997	6.445	22.202	310.00	0.494	-0.8	0.017	347.7
	K	20.8	3.209	0.999	4.246	19.175	86.35	0.651	-0.9	0.027	326.9
	Na	20.8	1.447	0.999	2.462	6.563	18.18	0.378	-0.8	0.011	661.1
34	Ca	87.7	5.715	2.400	17.251	133.18	1102.6	0.916	-3.9	0.063	345.2
	K	87.7	9.999	1.200	14.012	176.48	2396.0	1.489	-4.2	0.174	-57.3
	Na	87.7	2.407	1.200	4.467	17.911	76.75	0.475	-3.4	0.017	6.2

† Theoretical moments according to Appendix C (third-type condition, layer 1):

$$M_1 = \frac{v^2}{L^2} C_o \left[\frac{t_o^2}{2} + Rt_o\left(\frac{D}{v^2} + \frac{x}{v}\right)\right]$$

$$M_2 = \frac{v^3}{L^3} C_o\left[\frac{t_o^3}{3} + Rt_o^2\left(\frac{D}{v^2} + \frac{x}{v}\right) + R^2t_o\left(4\frac{D^2}{v^4} + 4\frac{xD}{v^3} + \frac{x^2}{v^2}\right)\right]$$

$$M_3 = \frac{v^4}{L^4} C_o\left[\frac{t_o^4}{4} + Rt_o^3\left(\frac{D}{v^2} + \frac{x}{v}\right) + R^2 \frac{t_o^2}{2}\left(12\frac{D^2}{v^4} + 12\frac{xD}{v^3} + 3\frac{x^2}{v^2}\right) + \right.$$
$$\left. + R^3t_o\left(30\frac{D^3}{v^6} + 30\frac{xD^2}{v^5} + 9\frac{x^2D}{v^4} + \frac{x^3}{v^3}\right)\right]$$

$$‡\ \mathrm{NLRT}=\left[\frac{(\mu'_1)_{\mathrm{experimental}} - (\mu'_1)_{\mathrm{theoretical}}}{(\mu'_1)_{\mathrm{theoretical}}} \times 100\%\right]$$

$$§\ \mathrm{NLSP}=\left[\frac{(\mu_2)_{\mathrm{experimental}} - (\mu_2)_{\mathrm{theoretical}}}{(\mu_2)_{\mathrm{theoretical}}} \times 100\%\right]$$

assumed that anion exchange obeyed a linear isotherm, although deviations from linear exchange would have a minimal effect on the value of D because the AEC is relatively small.

Table 16 also contains values for the first absolute moment, μ'_1, and the second central moment, μ_2. To assess the influence of non-linear exchange on breakthrough time and spreading, the relative differences between theoretical (table 16) and experimental (table 15) values for μ'_1 and μ_2 are included as NLRT and NLSP, respectively. One can view this as the error made by obtaining D and R under the assumption of linear exchange. Positive values of NLRT and NLSP indicate that the experimentally obtained parameter value overestimates the "correct" theoretical value.

The results for experiment 31 are not very reliable because of the high values for D, which were attributed to non-equilibrium conditions, possibly because of poor packing (cf. figure 14). For the other experiments, no large deviations between experimental and theoretical values were found for μ'_1, as indicated by the low values for NLRT. Apparently, the difference in mean residence time for linear and non-linear exchange is small. However, substantial differences in values for μ_2 occurred, as pointed out by the high values for NLSP. The theoretical values for μ_2 do not account for non-linear exchange, whereas the experimental μ_2 values (implicitly) include all mechanisms contributing to spreading. Because the soil in each column was fairly uniform, this difference was attributed to non-linear exchange. The non-linearity increased solute spreading for all cations with the exception of K during experiment 34. The μ_2 values for Na were most affected, with the exception of experiment 34. A similar comparison can be made for D. The adjusted (theoretical) values for D during ternary exchange represent only hydrodynamic dispersion (table 16), whereas the experimental values for D account for both hydrodynamic dispersion and non-linear exchange (table 15).

The influence of non-linear exchange on R was already demonstrated in tables 14 and 15. Because K is adsorbed more favorably than Na, it is retarded two to four times more than Na. It seems that this is the most important effect non-linear exchange has on solute transport. This effect becomes more pronounced when the equivalents of solute applied as a pulse are small relative to the total equivalents in the adsorbed and liquid phases.

SUMMARY AND CONCLUSIONS

Breakthrough curves were determined in four types of experiments, namely (1) a pilot study involving step displacement in homogeneous soil columns of 30 cm length, (2) step displacement in layered soils, (3) pulse displacement in soil columns of 15 cm length with binary exchange, and (4) pulse displacement in soil columns of 15 cm length for ternary exchange. Results of the pilot study indicated that approximative methods based on Eq.(7) yield fairly reliable values for D and R and that curve fitting may produce erroneous results if too many unknowns need to be fitted (e.g., non-equilibrium model). The step displacement experiments in layered media yielded symmetrical and steep BTC's.

Changes in total solute concentration in the effluent during simultaneous anion and cation displacement were insufficient to conclude that the CEC varied during the application of a Na pulse to a Ca soil. Transport parameters determined from anion displacement were used to study the effect of non-linear exchange on cation displacement. Ternary displacement experiments demonstrated differences in retardation and dispersion due to non-linear exchange. The Na pulse moved two to four times faster through the soil than the K pulse.

The determination of R was illustrated graphically for pulse and step input. Calculated results were presented using column holdup and the ratio of residence time of solute and solvent. Statistical moments with respect to time were used to analyze the BTC's for pulse displacement. Theoretical moments, derived from the ADE for four cases, seem to be very useful to determine parameters for arbitrary transport models. The theoretical moments showed that more retardation and dispersion occurred for a third-type condition than for a first-type condition. Layering only affects spreading and dispersion by changes in magnitude of the transport parameters. No interface effects occur, however, and the layered medium is actually a series of homogeneous media.

The theoretical moments were also used to interpret experimental data. The determination of R yielded reliable results, whereas the determination of D was inaccurate for binary systems. The reliability can be improved by using longer columns or by determining BTC's at more than one position. The values of the (theoretical) moments were determined based on transport parameters obtained from anion displacement. Comparison of theoretical and experimental moments for cation displacement helped quantify the effect of non-linear exchange on dispersion and retardation. In particular, the value for R, which determines the residence time, was affected by non-linear exchange. If solute movement needs to be simulated, it is worthwhile to first obtain reliable values for R under similar circumstances. However, values for D are affected as well by non-linear exchange: D values obtained from experiments involving ternary (non-linear) exchange were up to ten times larger than their corresponding values when hydrodynamic dispersion was singled out as the sole process determining D.

The following guideline is offered for quick prediction of solute movement during equilibrium conditions, beginning with the most important steps. First, determine the R values for the various solutes. If BTC's are available, this determinatioin is conveniently done with the methods outlined in the section on the graphical determination of R. Otherwise, values for the CEC, determined under conditions similar to those for which transport needs to be predicted, can be used. Second, the value for D must be determined to quantify hydrodynamic dispersion. This determination can be done relatively fast with non-reactive solutes, using approximative methods or with curve fitting. If more time is available, experiments involving both non-reactive and reactive solutes are to be preferred to determine D with the BTC for the non-reactive solute, and an effective value for R with the reactive solute. If the BTC is determined at two positions or exhibits sufficient spreading, as for our ternary systems, the data are conveniently analyzed with the method of moments. Third, for reactive solutes, the exchange isotherm should be determined if a good prediction of R is needed and sufficient time is available. This last step is not needed for trace amounts of solute or for incomplete exchange.

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APPENDIX A

Analytical Solution of the ADE for a Pulse Input with a First- and Third-type Condition in a Two-layer Medium

1. First layer

It is assumed that the first layer is in effect semi-infinite and homogeneous with respect to the flow and transport properties. The transport problem for which we seek a solution can be stated as follows:

$$\frac{\partial C}{\partial t} = D_1 \frac{\partial^2 C}{\partial x^2} - v_1 \frac{\partial C}{\partial x} \qquad t>0 \qquad 0<x<L_1 \qquad \text{(A-1)}$$

$$C(x,0) = 0 \qquad 0<x<L_1 \qquad \text{(A-2-a)}$$

$$C(0,t) = f(t) \qquad \text{(first-type)} \qquad t>0 \qquad \text{(A-2-b)}$$

$$\left[-D_1 \frac{\partial C}{\partial x} + v_1 C\right]_{x=0} = v_1 f(t) \qquad \text{(third-type)} \qquad t>0 \qquad \text{(A-2-c)}$$

$$f(t) = \begin{cases} C_o & 0<t\leq t_o \\ 0 & t>t_o \end{cases} \qquad \text{(A-2-d)}$$

$$\left.\frac{\partial C}{\partial x}\right|_{x\to\infty} = 0 \qquad t>0 \qquad \text{(A-2-e)}$$

Solution of Eq.(A-1), subject to Eq.(A-2), can be achieved with the help of Laplace transforms. The transformed equation and boundary conditions are:

$$\frac{d^2\bar{C}}{dx^2} - \frac{v_1}{D_1}\frac{d\bar{C}}{dx} - \frac{s}{D_1}\bar{C} = 0 \qquad 0<x<L_1 \qquad \text{(A-3)}$$

$$\bar{C}(0,s) = \bar{f}(s) \qquad \text{(A-4-a)}$$

$$\left[-D_1 \frac{d\bar{C}}{dx} + v_1 \bar{C}\right]_{x=0} = v_1 \bar{f}(s) \qquad \text{(A-4-b)}$$

$$\left.\frac{d\bar{C}}{dx}\right|_{x\to\infty} = 0 \qquad \text{(A-4-c)}$$

where s is the transformation variable and $\bar{C}$ and $\bar{f}$ are given by:

$$\bar{C}(x,s) = \int_0^\infty e^{-st}\, C(x,t)\, dt \tag{A-5}$$

$$\bar{f}(s) = \int_0^\infty e^{-st}\, f(t)\, dt = \frac{C_o}{s}\,(1-exp(-st_o)) \tag{A-6}$$

The general solution of the ordinary differential equation, Eq.(A-3), can be written as:

$$\bar{C}(x,s) = \alpha\; exp(\lambda_1^+ x) + \beta\; exp(\lambda_1^- x) \tag{A-7}$$

where $\lambda_1^{\pm} = \frac{v_1}{2D_1} \pm \sqrt{\left[\frac{v_1}{2D_1}\right]^2 + \frac{s}{D_1}}$, and α and β are coefficients depending on the boundary conditions. According to Eq.(A-4-c) α is equal to 0 and we denote λ_1^- as λ_1. The use of Eq.(A-4-a) or (A-4-b) allows the evaluation of β:

$$\beta = \bar{f}(s) \qquad \text{(first-type)} \tag{A-8-a}$$

$$\beta = \frac{v_1 \bar{f}(s)}{(v_1 - D_1\lambda_1)} \qquad \text{(third-type)} \tag{A-8-b}$$

Substitution of these expressions for β into Eq. (A-7) results in the following solutions:

$$\bar{C}(x,s) = \frac{C_o}{s}\,(1-exp(-st_o))\; exp(\lambda_1 x) \qquad \text{(first-type)} \tag{A-9-a}$$

$$\bar{C}(x,s) = \frac{v_1 C_o}{s}\,\frac{(1-exp(-st_o))}{v_1 - D_1\lambda_1}\; exp(\lambda_1 x) \qquad \text{(third-type)} \tag{A-9-b}$$

2. Second layer

The solution of the concentration in a (uniform) second layer ($L<x<\infty$) is very similar to the solution for a non-layered uniform soil. We assume that the concentration in the first layer ($0<x<L_1$) is accurately described with Eq.(A-9-a) and (A-9-b) for a first- and third-type inlet condition, respectively. We wish to solve:

$$\frac{\partial C}{\partial t} = D_2 \frac{\partial^2 C}{\partial x^2} - v_2 \frac{\partial C}{\partial x} \qquad t>0 \qquad L_1<x<\infty \qquad \text{(A-10)}$$

subject to:

$$C(x,0) = 0 \qquad L_1<x<\infty \qquad \text{(A-11-a)}$$

$$C\Big|_{x\downarrow L_1} = C\Big|_{x\uparrow L_1} \qquad \text{(first-type)} \qquad t>0 \qquad \text{(A-11-b)}$$

$$\left[-\theta_2 D_2 \frac{\partial C}{\partial x} + \theta_2 v_2 C\right]_{x\downarrow L_1} = \left[-\theta_1 D_1 \frac{\partial C}{\partial x} + \theta_1 v_1 C\right]_{x\uparrow L_1} \qquad \text{(A-11-c)}$$

$$\text{(third-type)} \qquad t>0$$

$$\left.\frac{\partial C}{\partial x}\right|_{x\to\infty} = 0 \qquad t>0 \qquad \text{(A-11-d)}$$

The Laplace transform is used in a similar manner as for the non-layered soil to obtain the solution of Eq.(A-10) subject to Eq.(A-11). The transformed equations are:

$$\frac{d^2\overline{C}}{dx^2} - \frac{v_2}{D_2}\frac{d\overline{C}}{dx} - \frac{s}{D_2}\overline{C} = 0 \qquad L_1<x<\infty \qquad \text{(A-12)}$$

$$\overline{C}\Big|_{x\downarrow L_1} = \overline{C}\Big|_{x\uparrow L_1} \qquad \text{(first-type)} \qquad \text{(A-13-a)}$$

$$\left[-\theta_2 D_2 \frac{d\overline{C}}{dx} + \theta_2 v_2 \overline{C}\right]_{x\downarrow L_1} = \left[-\theta_1 D_1 \frac{d\overline{C}}{dx} + \theta_1 v_1 \overline{C}\right]_{x\uparrow L_1} \qquad \text{(A-13-b)}$$

$$\text{(third-type)}$$

$$\left.\frac{d\bar{C}}{dx}\right|_{x\to\infty} = 0 \qquad \text{(A-13-c)}$$

where the concentration at the end of the first layer ($x\uparrow L_1$) is given by:

$$\bar{C}(L_1,s) = \bar{f}\ \mathit{exp}(\lambda_1 L_1) \qquad \text{(first-type)} \qquad \text{(A-14-a)}$$

$$\bar{C}(L_1,s) = \frac{v_1\bar{f}}{v_1-D_1\lambda_1}\ \mathit{exp}(\lambda_1 L_1) \qquad \text{(third-type)} \qquad \text{(A-14-b)}$$

The general solution of Eq.(A-12) is:

$$\bar{C}(x,s) = \alpha\ \mathit{exp}(\lambda_2^{+}x) + \beta\ \mathit{exp}(\lambda_2^{-}x) \qquad \text{(A-15)}$$

where $\lambda_2^{\pm} = \frac{v_2}{2D_2} \pm \sqrt{\left[\frac{v_2}{2D_2}\right]^2 + \frac{s}{D_2}}$, and α and β are again coefficients determined by the boundary conditions. From Eq.(A-13-c) we conclude that $\alpha=0$. Eq.(A-13-a) and (A-13-b) are used to evaluate β for a first and third-type condition, respectively:

$$\beta = \bar{f}\ \mathit{exp}((\lambda_1-\lambda_2)L_1) \qquad \text{(first-type)} \qquad \text{(A-16-a)}$$

$$\beta = \frac{\theta_1}{\theta_2}\ \frac{v_1\bar{f}}{v_2-D_2\lambda_2}\ \mathit{exp}((\lambda_1-\lambda_2)L_1) \qquad \text{(third-type)} \qquad \text{(A-16-b)}$$

where $\lambda_2=\lambda_2^{-}$. This leads to the following respective solutions:

$$\bar{C}(x,s) = \bar{f}\ \mathit{exp}(\lambda_1 L_1+\lambda_2\xi) \qquad \text{(first-type)} \qquad \text{(A-17-a)}$$

$$\bar{C}(x,s) = \frac{\theta_1}{\theta_2}\ \frac{v_1\bar{f}}{v_2-D_2\lambda_2}\ \mathit{exp}(\lambda_1 L_1+\lambda_2\xi) \qquad \text{(third-type)} \qquad \text{(A-17-b)}$$

where $\xi=x-L_1$.

APPENDIX B

Derivation of Moments Based on Analytical Solutions of the ADE in the Laplace Domain

The p-th moment of a time dependent concentration distribution, for a fixed position, is defined by:

$$m_p = \int_0^\infty t^p \, C(x,t) \, dt \qquad p=0,1,2,.... \qquad \text{(B-1)}$$

The concentration distribution, C(x,t), can be determined theoretically or experimentally. However, explicit analytical solutions for C(x,t) are sometimes not readily available. Aris *(3)* showed how m_p can be obtained if a solution, $\bar{C}(x,s)$, in the Laplace domain is known. This solution is obtained rather easily in comparison with the regular solution. According to Aris *(3)*, the p-th moment in the Laplace domain is given by:

$$m_p = (-1)^p \lim_{s \to 0} \frac{d^p}{ds^p} \left[\bar{C}(x,s) \right] \qquad \text{(B-2)}$$

The procedure of differentiation and limitation is rather straightforward, but becomes tedious for the higher moments as noted by Valocchi *(21)*. To illustrate the use of Eq.(B-2), we will determine m_0 for a non-layered soil using a third-type inlet condition. The solution in the Laplace domain is given by Eq.(A-9-b). From Eq.(B-2) we get ($s=0$: $\lambda_1=0$):

$$m_0 = \lim_{s\to 0}\left[\frac{v_1 C_o}{s}\,\frac{(1-exp(-st_o))}{v_1 - D_1\lambda_1}\,exp(\lambda_1 x)\right] = C_o \lim_{s\to 0}\left[\frac{1-exp(-st_o)}{s}\right] \qquad \text{(B-3)}$$

The indeterminate form is evaluated with l'Hôpital's rule. Both numerator and denominator tend to go to 0 if s→0. Because the ratio of their derivatives is t_o for s→0, we have:

$$m_0 = C_o t_o \qquad \text{(B-4)}$$

The zeroth moment is proportional to the total amount of mass applied during a pulse. The evaluation of moments of higher order is done in a similar manner.

APPENDIX C

Time Moments m, μ', and μ for BTC's as a Result of a Pulse Input During Steady Flow in a Medium with One or Two Layeres with a First- or Third-type Inlet Condition†

m_0	A	$C_o t_o$
	B	$C_o t_o$
	C	$C_o t_o$
	D	$C_o t_o$
m_1	A	$C_o\left[\frac{t_o^2}{2} + \frac{x}{v_1} t_o\right]$
	B	$C_o\left[\frac{t_o^2}{2} + t_o\left(\frac{D_1}{v_1^2} + \frac{x}{v_1}\right)\right]$
	C	$C_o\left[\frac{t_o^2}{2} + t_o\left(\frac{L_1}{v_1} + \frac{\xi}{v_2}\right)\right]$
	D	$C_o\left[\frac{t_o^2}{2} + t_o\left(\frac{D_2}{v_2^2} + \frac{L_1}{v_1} + \frac{\xi}{v_2}\right)\right]$
m_2	A	$C_o\left[\frac{t_o^3}{3} + t_o^2\frac{x}{v_1} + t_o\left(2\frac{xD_1}{v_1^3} + \frac{x^2}{v_1^2}\right)\right]$
	B	$C_o\left[\frac{t_o^3}{3} + t_o^2\left(\frac{D_1}{v_1^2} + \frac{x}{v_1}\right) + t_o\left(4\frac{D_1^2}{v_1^4} + 4\frac{xD_1}{v_1^3} + \frac{x^2}{v_1^2}\right)\right]$
	C	$C_o\left[\frac{t_o^3}{3} + t_o^2\left(\frac{L_1}{v_1} + \frac{\xi}{v_2}\right) + t_o\left(2\frac{L_1D_1}{v_1^3} + 2\frac{\xi D_2}{v_2^3} + \frac{L_1^2}{v_1^2} + \frac{\xi^2}{v_2^2} + 2\frac{L_1\xi}{v_1v_2}\right)\right]$
	D	$C_o\left[\frac{t_o^3}{3} + t_o^2\left(\frac{D_2}{v_2^2} + \frac{L_1}{v_1} + \frac{\xi}{v_2}\right) + t_o\left\{4\frac{D_2^2}{v_2^4} + 2\frac{D_2}{v_2^2}\left(\frac{L_1}{v_1} + \frac{\xi}{v_2}\right) +\right.\right.$ $\left.\left.2\frac{L_1D_1}{v_1^3} + 2\frac{\xi D_2}{v_2^3} + 2\frac{L_1\xi}{v_1v_2} + \frac{L_1^2}{v_1^2} + \frac{\xi^2}{v_2^2}\right\}\right]$

---

†Cases are listed in table 1.

APPENDIX C. Continued.

m_3 A $$C_o\left[\frac{t_o^4}{4} + t_o^3\frac{x}{v_1} + \frac{t_o^2}{2}\left(6\frac{xD_1}{v_1^3} + 3\frac{x^2}{v_1^2}\right) + t_o\left(12\frac{xD_1^2}{v_1^5} + 6\frac{x^2D_1}{v_1^4} + \frac{x^3}{v_1^3}\right)\right]$$

B $$C_o\left[\frac{t_o^4}{4} + t_o^3\left(\frac{D_1}{v_1^2} + \frac{x}{v_1}\right) + \frac{t_o^2}{2}\left(12\frac{D_1^2}{v_1^4} + 12\frac{xD_1}{v_1^3} + 3\frac{x^2}{v_1^2}\right) + \right.$$

$$\left. + t_o\left(30\frac{D_1^3}{v_1^6} + 30\frac{xD_1^2}{v_1^5} + 9\frac{x^2D_1}{v_1^4} + \frac{x^3}{v_1^3}\right)\right]$$

C $$C_o\left[\frac{t_o^4}{4} + t_o^3\left(\frac{L_1}{v_1} + \frac{\xi}{v_2}\right) + \frac{t_o^2}{2}\left(6\frac{L_1D_1}{v_1^3} + 3\frac{L_1^2}{v_1^2} + 6\frac{L_1\xi}{v_1v_2} + 3\frac{\xi^2}{v_2^2} + 6\frac{\xi D_2}{v_2^3}\right) + \right.$$

$$+ t_o\left(12\frac{L_1D_1^2}{v_1^5} + 6\frac{L_1^2D_1}{v_1^4} + \frac{L_1^3}{v_1^3} + 6\frac{L_1\xi D_1}{v_1^3v_2} + 3\frac{L_1^2\xi}{v_1^2v_2} + 12\frac{\xi D_2^2}{v_2^5} + 6\frac{\xi^2D_2}{v_2^4} + \right.$$

$$\left.\left. + \frac{\xi^3}{v_2^3} + 6\frac{L_1\xi D_2}{v_1v_2^3} + 3\frac{L_1\xi^2}{v_1v_2^2}\right)\right]$$

D $$C_o\left[\frac{t_o^4}{4} + t_o^3\left(\frac{D_2}{v_2^2} + \frac{L_1}{v_1} + \frac{\xi}{v_2}\right) + \frac{t_o^2}{2}\left(12\frac{D_2^2}{v_2^4} + 6\frac{L_1D_2}{v_1v_2^2} + 12\frac{\xi D_2}{v_2^3} + \right.\right.$$

$$\left. 6\frac{L_1D_1}{v_1^3} + 6\frac{L_1\xi}{v_1v_2} + 3\frac{L_1^2}{v_1^2} + 3\frac{\xi^2}{v_2^2}\right) + t_o\left\{30\frac{D_2^2}{v_2^6} + 30\frac{\xi D_2^2}{v_2^5} + 12\frac{L_1D_2^2}{v_1v_2^4} + \right.$$

$$+ 9\frac{\xi^2D_2}{v_2^4} + 12\frac{L_1\xi D_2}{v_1v_2^3} + \frac{\xi^3}{v_2^3} + 6\frac{L_1D_1D_2}{v_1^3v_2^2} + 3\frac{L_1^2D_2}{v_1^2v_2^2} + 3\frac{L_1\xi^2}{v_1v_2^2} + 6\frac{L_1\xi D_1}{v_1^3v_2} +$$

$$\left.\left. + 3\frac{L_1^2\xi}{v_1^2v_2} + \frac{L_1^3}{v_1^3} + 6\frac{L_1^2D_1}{v_1^4} + 12\frac{L_1D_1^2}{v_1^5}\right\}\right]$$

APPENDIX C. Continued.

μ'_1	A	$\frac{t_o}{2} + \frac{x}{v_1}$
	B	$\frac{t_o}{2} + \frac{D_1}{v_1^2} + \frac{x}{v_1}$
	C	$\frac{t_o}{2} + \frac{L_1}{v_1} + \frac{\xi}{v_2}$
	D	$\frac{t_o}{2} + \frac{D_2}{v_2^2} + \frac{L_1}{v_1} + \frac{\xi}{v_2}$
μ'_2	A	$\frac{t_o^2}{3} + t_o \frac{x}{v_1} + 2\frac{xD_1}{v_1^3} + \frac{x^2}{v_1^2}$
	B	$\frac{t_o^2}{3} + t_o\left(\frac{D_1}{v_1^2} + \frac{x}{v_1}\right) + 4\frac{D_1^2}{v_1^4} + 4\frac{xD_1}{v_1^3} + \frac{x^2}{v_1^2}$
	C	$\frac{t_o^2}{3} + t_o\left(\frac{L_1}{v_1} + \frac{\xi}{v_2}\right) + 2\frac{L_1D_1}{v_1^3} + 2\frac{\xi D_2}{v_2^3} + \frac{L_1^2}{v_1^2} + \frac{\xi^2}{v_2^2} + 2\frac{L_1\xi}{v_1v_2}$
	D	$\frac{t_o^2}{3} + t_o\left(\frac{D_2}{v_2^2} + \frac{L_1}{v_1} + \frac{\xi}{v_2}\right) + 4\frac{D_2^2}{v_2^4} + 4\frac{\xi D_2}{v_2^3} + \frac{\xi^2}{v_2^2} + 2\frac{L_1\xi}{v_1v_2} + \frac{L_1^2}{v_1^2} + 2\frac{L_1D_2}{v_1v_2^2} + 2\frac{L_1D_1}{v_1^3}$
μ'_3	A	$\frac{t_o^3}{4} + t_o^2 \frac{x}{v_1} + \frac{t_o}{2}\left(6\frac{xD_1}{v_1^3} + 3\frac{x^2}{v_1^2}\right) + 12\frac{xD_1^2}{v_1^5} + 6\frac{x^2D_1}{v_1^4} + \frac{x^3}{v_1^3}$
	B	$\frac{t_o^3}{4} + t_o^2\left(\frac{D_1}{v_1^2} + \frac{x}{v_1}\right) + \frac{t_o}{2}\left(12\frac{D_1^2}{v_1^4} + 12\frac{xD_1}{v_1^3} + 3\frac{x^2}{v_1^2}\right) + 30\frac{D_1^3}{v_1^6} + 30\frac{xD_1^2}{v_1^5} + 9\frac{x^2D_1}{v_1^4} + \frac{x^3}{v_1^3}$

APPENDIX C. Continued.

C $$\frac{t_o^3}{4} + t_o^2\left(\frac{L_1}{v_1} + \frac{\xi}{v_2}\right) + \frac{t_o}{2}\left(6\frac{L_1D_1}{v_1^3} + 3\frac{L_1^2}{v_1^2} + 6\frac{L_1\xi}{v_1v_2} + 3\frac{\xi^2}{v_2^2} + 6\frac{\xi D_2}{v_2^3}\right) +$$

$$+ 12\frac{L_1D_1^2}{v_1^5} + 6\frac{L_1^2D_1}{v_1^4} + \frac{L_1^3}{v_1^3} + 6\,\frac{L_1\xi D_1}{v_1^3v_2} + 3\frac{L_1^2\xi}{v_1^2v_2} + 12\frac{\xi D_2^2}{v_2^5} +$$

$$+ 6\frac{\xi^2D_2}{v_2^4} + \frac{\xi^3}{v_2^3} + 6\frac{L_1\xi D_2}{v_1v_2^3} + 3\frac{L_1\xi^2}{v_1v_2^2}$$

D $$\frac{t_o^3}{4} + t_o^2\left(\frac{D_2}{v_2^2} + \frac{L_1}{v_1} + \frac{\xi}{v_2}\right) + \frac{t_o}{2}\left(12\frac{D_2^2}{v_2^4} + 6\frac{L_1D_2}{v_1v_2^2} + 12\frac{\xi D_2^2}{v_2^3} + 6\frac{L_1D_1}{v_1^3} +\right.$$

$$\left. + 6\frac{L_1\xi}{v_1v_2} + 3\frac{L_1^2}{v_1^2} + 3\frac{\xi^2}{v_2^2}\right) + 30\frac{D_2^3}{v_2^6} + 30\frac{\xi D_2^2}{v_2^5} + 12\frac{L_1D_2^2}{v_1v_2^4} + 9\frac{\xi^2D_2}{v_2^4} +$$

$$+ 12\frac{L_1\xi D_2}{v_1v_2^3} + \frac{\xi^3}{v_2^3} + 6\frac{L_1D_1D_2}{v_1^3v_2^2} + 3\frac{L_1^2D_2}{v_1^2v_2^2} + 3\frac{L_1\xi^2}{v_1v_2^2} + 6\frac{L_1\xi D_1}{v_1^3v_2} + 3\frac{L_1^2\xi}{v_1^2v_2} +$$

$$+ \frac{L_1^3}{v_1^3} + 6\,\frac{L_1^2D_1}{v_1^4} + 12\frac{L_1D_1^2}{v_1^5}$$

APPENDIX C. Continued.

μ_1	A	0
	B	0
	C	0
	D	0
μ_2	A	$\frac{t_o^2}{12} + 2\frac{xD_1}{v_1^3}$
	B	$\frac{t_o^2}{12} + 3\frac{D_1^2}{v_1^4} + 2\frac{xD_1}{v_1^3}$
	C	$\frac{t_o^2}{12} + 2\frac{L_1D_1}{v_1^3} + 2\frac{\xi D_2}{v_2^3}$
	D	$\frac{t_o^2}{12} + 3\frac{D_2^2}{v_2^4} + 2\frac{L_1D_1}{v_1^3} + 2\frac{\xi D_2}{v_2^3}$
μ_3	A	$\frac{t_o^3}{24} + \frac{t_o^2}{12}\frac{x}{v_1} + t_o\left[2\frac{xD_1}{v_1^3} + \frac{x^2}{v_1^2}\right] + 12\frac{xD_1^2}{v_1^5} + 2\frac{x^2D_1}{v_1^4}$
	B	$\frac{t_o^3}{24} + \frac{t_o^2}{12}\left[\frac{D_1}{v_1^2} + \frac{x}{v_1}\right] + \frac{t_o}{2}\left[3\frac{D_1^2}{v_1^4} + 2\frac{xD_1}{v_1^3}\right] + 23\frac{D_1^3}{v_1^6} + 17\frac{xD_1^2}{v_1^5} + 2\frac{x^2D_1}{v_1^4}$
	C	$\frac{t_o^3}{24} + \frac{t_o^2}{12}\left[\frac{L_1}{v_1} + \frac{\xi}{v_2}\right] + t_o\left[\frac{L_1D_1}{v_1^3} + \frac{\xi D_2}{v_2^3}\right] + 12\frac{L_1D_1^2}{v_1^5} + 2\frac{L_1^2D_1}{v_1^4} +$ $+ 2\frac{\xi L_1D_1}{v_2v_1^3} + 12\frac{\xi D_2^2}{v_2^5} + 2\frac{\xi^2D_2}{v_2^4} + 2\frac{L_1\xi D_2}{v_1v_2^3}$
	D	$\frac{t_o^3}{24} + \frac{t_o^2}{12}\left[\frac{D_2}{v_2^2} + \frac{L_1}{v_1} + \frac{\xi}{v_2}\right] + \frac{t_o}{2}\left[3\frac{D_2^2}{v_2^4} + 2\frac{\xi D_2}{v_2^3} + 2\frac{L_1D_1}{v_1^3}\right] + 23\frac{D_2^2}{v_2^6} +$ $+ 17\frac{\xi D_2^2}{v_2^5} + 3\frac{L_1D_2^2}{v_1v_2^4} + 3\frac{\xi^2D_2}{v_2^4} + 2\frac{L_1\xi D_2}{v_1v_2^3} + 2\frac{L_1D_1D_2}{v_1^3v_2^2} + \frac{L_1^2D_2}{v_1^2v_2^2} + 2\frac{L_1\xi D_1}{v_1^3v_2} +$ $+ 2\frac{L_1^2D_1}{v_1^4} + 12\frac{L_1D_1^2}{v_1^5}$

APPENDIX D

Input Files for the Program CXTFIT Containing the Experimentally Determined C/C_o-profiles

The first column of each file contains values for C/C_o, the second column lists the value of the distance (column length, L) and the third column contains the number of pore volumes, T. Length is expressed in cm and time in days, with the exception of experiments 1-6 where the time is given in minutes. Further details are provided by Parker and van Genuchten *(13)*.

Experiment 1: Calcium

```
       4        1        2        30        29        0        0
SAND SATURATED WITH 0.1 M CACL2, DISPLACEMENT WITH SALT FREE WATER
DBD=1.92 g/cm3 VMC=0.28 PV=173 cm3 V=0.839 cm/min       1-Ca
    V.....       D....      R....      To...     RX1..     RX0..
   0.8388         0.1        1.0        0.0       0.5       0.5
        0           1          1          0         1         1
      1.0         0.0
      0.0        30.6     0.0549
      0.0        30.6     0.1919
      0.0        30.6     0.3290
      0.0        30.6     0.4661
      0.0        30.6     0.6032
      0.0        30.6     0.7403
      0.0        30.6     0.8225
      0.0        30.6     0.8774
      0.0        30.6     0.9048
    0.012        30.6     0.9871
    0.056        30.6     1.0145
    0.132        30.6     1.0420
    0.234        30.6      1.070
    0.381        30.6      1.097
    0.519        30.6      1.125
    0.651        30.6      1.152
    0.753        30.6      1.179
    0.830        30.6      1.207
    0.882        30.6      1.234
    0.918        30.6      1.262
    0.943        30.6      1.289
    0.957        30.6      1.317
    0.967        30.6      1.344
    0.973        30.6      1.371
    0.978        30.6      1.399
    0.981        30.6      1.426
    0.984        30.6      1.454
    0.985        30.6      1.481
    0.987        30.6      1.536
```

Experiment 2: Calcium

```
       4        1        2        30        24        0        0
SAND SATURATED WITH 0.1 M CACL2, DISPLACEMENT WITH SALT FREE WATER
DBD=1.91 g/cm3 VMC=0.28 PV=175 cm3 V=0.906 cm/min
    V.....       D....      R....      To...     RX1..     RX0..
   0.9056         0.1        1.0        0.0       0.5       0.5
        0           1          1          0         1         1
      1.0         0.0
      0.0        30.6      0.089
      0.0        30.6      0.237
      0.0        30.6      0.385
      0.0        30.6      0.533
      0.0        30.6      0.681
      0.0        30.6      0.829
    0.003        30.6      0.977
    0.031        30.6      1.006
    0.092        30.6      1.036
    0.213        30.6      1.065
    0.362        30.6      1.095
    0.507        30.6      1.125
    0.643        30.6      1.154
    0.758        30.6      1.184
    0.836        30.6      1.213
    0.890        30.6      1.243
    0.925        30.6      1.273
    0.946        30.6      1.302
    0.968        30.6      1.332
    0.976        30.6      1.391
    0.980        30.6      1.450
    0.983        30.6      1.509
    0.986        30.6      1.568
    0.987        30.6      1.598
```

Experiment 3: Bromide and Chloride

```
 1
 4           1        2       30      18      0        0
PRATTVILLE (upper); DISPLACEMENT OF 0.01 M CACL2 BY 0.01 M CABR2:
BR-   CONCENTRATION   PV=250.6 cm3  DBD=1.58 g/cm3   VMC=0.402
    V....       D....       R....      To...     RX1..     RX0..
 0.012360        0.1         1.0       10.0       0.5       0.5
        0          1           1          0         1         1
      0.0        1.0
    0.000       30.6       0.085
    0.000       30.6       0.242
    0.000       30.6       0.389
    0.090       30.6       0.493
    0.163       30.6       0.537
    0.291       30.6       0.610
    0.390       30.6       0.679
    0.547       30.6       0.820
    0.658       30.6       0.966
    0.695       30.6       1.089
    0.726       30.6       1.122
    0.794       30.6       1.296
    0.852       30.6       1.478
    0.861       30.6       1.532
    0.902       30.6       1.657
    0.910       30.6       1.829
    0.947       30.6       1.996
```

```
 1
 4           1        2
PRATTVILLE (upper); DISPLACEMEN
(1-Cl)CONCENTRATION   PV=250.6
    V....       D....       R....
 0.012360        0.1         1.0
        0          1           1
      0.0        1.0
    0.000       30.6       0.085
    0.005       30.6       0.242
    0.005       30.6       0.389
    0.065       30.6       0.493
    0.149       30.6       0.537
    0.265       30.6       0.610
    0.375       30.6       0.679
    0.431       30.6       0.820
    0.533       30.6       0.966
    0.649       30.6       1.089
    0.699       30.6       1.122
    0.767       30.6       1.296
    0.821       30.6       1.478
    0.856       30.6       1.532
    0.859       30.6       1.657
    0.885       30.6       1.829
    0.913       30.6       1.996
    0.938       30.6       2.164
```

Experiment 4: Bromide and Chloride

```
 1
 4           1        2       30      15      0        0
PRATTVILLE (upper) ; DISPLACEMENT OF  0.01 M CACL2 BY 0.01 M CABR2:
BR   CONCENTRATION PV=249.0 cm3 DBD=1.59 g/cm3 VMC=0.4 units:cm,min,g
    V....       D....       R....      To...     RX1..     RX0..
 0.047330        0.1         1.0        10.       0.5       0.5
        0          1           1          0         1         1
      0.0        1.0
      0.0       30.6       0.083
    0.000       30.6       0.242
    0.045       30.6       0.399
    0.155       30.6       0.480
    0.245       30.6       0.557
    0.395       30.6       0.714
    0.508       30.6       0.841
    0.639       30.6       1.022
    0.731       30.6       1.175
    0.789       30.6       1.330
    0.862       30.6       1.476
    0.908       30.6       1.621
    0.958       30.6       1.771
    0.965       30.6       1.923
    0.984       30.6       2.076
```

```
 1
 4           1        2
PRATTVILLE (upper) ; DISPLACEME
1-Cl-CONCENTRATION PV=249.0 cm3
    V....       D....       R....
 0.047330        0.1         1.0
        0          1           1
      0.0        1.0
      0.0       30.6       0.083
    0.006       30.6       0.242
    0.065       30.6       0.399
    0.132       30.6       0.480
    0.229       30.6       0.557
    0.396       30.6       0.714
    0.482       30.6       0.841
    0.627       30.6       1.022
    0.709       30.6       1.175
    0.777       30.6       1.330
    0.832       30.6       1.476
    0.891       30.6       1.621
    0.915       30.6       1.771
    0.901       30.6       1.923
    0.958       30.6       2.076
```

Experiment 5: Bromide and Chloride

```
 1
 4           1        2       30      17      0        0
PBU; DISPLACEMENT OF 0.01 M CACL2 BY 0.01 M CABR2 (units cm, min)
PV=285.7 cm3, DBD=1.433 g/cm3  VMC=0.459     BR
    V....       D....       R....      To...     RX1..     RX0..
 0.005972        0.1         1.0      1.925       0.5       0.5
        0          1           1          0         1         1
      0.0        1.0
      0.0       30.6       0.055
      0.0       30.6       0.167
    0.000       30.6       0.281
    0.000       30.6       0.394
    0.009       30.6       0.505
    0.017       30.6       0.646
    0.086       30.6       0.735
    0.237       30.6       0.855
    0.440       30.6       0.974
    0.668       30.6       1.092
    0.821       30.6       1.214
    0.894       30.6       1.313
    0.967       30.6       1.379
    0.964       30.6       1.499
    0.971       30.6       1.595
    0.974       30.6       1.741
    0.976       30.6       1.925
```

```
 1
 4           1        2
PBU; DISPLACEMENT OF 0.01 M CA(
PV=285.7 cm3, DBD=1.433 g/cm3
    V....       D....       R....
 0.005972        0.1         1.0
        0          1           1
      0.0        1.0
      0.0       30.6       0.055
      0.0       30.6       0.167
    0.006       30.6       0.281
    0.001       30.6       0.394
    0.015       30.6       0.505
    0.063       30.6       0.646
    0.121       30.6       0.735
    0.222       30.6       0.855
    0.392       30.6       0.974
    0.542       30.6       1.092
    0.747       30.6       1.214
    0.852       30.6       1.313
    0.894       30.6       1.379
    0.947       30.6       1.499
    0.950       30.6       1.595
    0.955       30.6       1.741
    0.995       30.6       1.925
```

Experiment 6: Bromide and Chloride

```
        1
        3          1          2          30          14          0          0
PBU; DISPLACEMENT OF 0.01 M CACL2 BY 0.01 M CABR2 (units cm, min, g)
PV=320.59 cm3, DBD=1.285 g/cm3, VMC=0.515   BR
    V....      D....      R....      To...      RX1..      RX0..
  0.18264       0.1        1.0      2.244        0.5        0.5
        0         1          1          0          1          1
      0.0       1.0
      0.0      30.6      0.120
    0.000      30.6      0.360
    0.000      30.6      0.598
    0.130      30.6      0.715
    0.246      30.6      0.832
    0.381      30.6      0.949
    0.541      30.6      1.067
    0.627      30.6      1.184
    0.729      30.6      1.301
    0.803      30.6      1.419
    0.873      30.6      1.536
    0.912      30.6      1.771
    0.926      30.6      2.007
    1.00      30.6      2.244
```

```
        1
        3          1          2
PBU; DISPLACEMENT OF 0.01 M CAC
PV=320.59 cm3, DBD=1.285 g/cm3,
    V....      D....      R....
  0.18264       0.1        1.0
        0         1          1
      0.0       1.0
      0.0      30.6      0.120
    0.024      30.6      0.360
    0.053      30.6      0.598
    0.131      30.6      0.715
    0.221      30.6      0.832
    0.337      30.6      0.949
    0.461      30.6      1.067
    0.564      30.6      1.184
    0.671      30.6      1.301
    0.739      30.6      1.419
    0.798      30.6      1.536
    0.850      30.6      1.771
    0.899      30.6      2.007
    0.934      30.6      2.244
```

Experiment 11: Calcium and Potassium

```
        1
        2          1          2          30          20          0          1
KBR    REPLACED BY CABR2;SOIL: SAN-WINI-SAN;WINI:0-250;SAN:250-500
P.V.:232.7;  CA          AGAINST P.V.; THETA=0.380;LARGE COLUMN 1
    V.....     D.....     R.....     TO....     rx1...     rx2...
   132.63        5.0        5.0     13.158          0          0
        0          1          1          0          0          0
      0.0        1.0
0.005      30.0      0.175
0.004      30.0      1.053
0.003      30.0      1.930
0.004      30.0      2.816
0.042      30.0      3.277
0.280      30.0      3.735
0.525      30.0      4.007
0.620      30.0      4.189
0.770      30.0      4.643
0.813      30.0      4.824
0.885      30.0      5.097
0.935      30.0      5.555
0.961      30.0      6.486
0.998      30.0      7.421
0.999      30.0      8.360
0.999      30.0      9.230
0.999      30.0      10.242
1.000      30.0      11.181
0.998      30.0      12.119
0.998      30.0      13.158
```

```
        1
        2          1
KBR    REPLACED BY CABR2;
P.V.:232.7;  K          A
    V.....     D.....     R
   132.63        1.0
        0          1
      0.0        1.0
0.000      30.0      0.175
0.000      30.0      1.053
0.021      30.0      1.930
0.024      30.0      2.816
0.067      30.0      3.277
0.301      30.0      3.735
0.543      30.0      4.007
0.633      30.0      4.189
0.775      30.0      4.643
0.828      30.0      4.824
0.885      30.0      5.097
0.948      30.0      5.555
0.970      30.0      6.486
0.980      30.0      7.421
0.985      30.0      8.360
0.987      30.0      9.230
0.989      30.0      10.242
0.991      30.0      11.181
0.993      30.0      12.119
0.994      30.0      13.158
```

Experiment 12: Calcium and Potassium

```
        1
        2         1        2        30        27        0       1
KBR    REPLACED BY CABR2;SOIL: 2 LAYER HEAII-HEAI;II:500-840;I:0-250;
P.V.:201.0;  ca          AGAINST P.V.; THETA=0.334;LARGE COLUMN 2
   V.....     D.....     R.....     TO....     rx1...     rx2...
   102.48        5.0        5.0   18.463          0          0
        0          1          1        0          0          0
      0.0        1.0
0.020      29.8      0.267
0.020      29.8      1.161
0.020      29.8      2.061
0.020      29.8      2.960
0.020      29.8      3.863
0.020      29.8      4.768
0.020      29.8      5.672
0.020      29.8      6.591
0.010      29.8      7.508
0.050      29.8      8.444
0.264      29.8      9.391
0.337      29.8      9.865
0.432      29.8      10.340
0.547      29.8      10.817
0.617      29.8      11.312
0.706      29.8      11.817
0.782      29.8      12.323
0.878      29.8      13.336
0.888      29.8      14.217
0.954      29.8      14.867
0.955      29.8      15.365
0.970      29.8      15.864
0.986      29.8      16.368
0.988      29.8      16.884
0.991      29.8      17.407
1.000      29.8      17.935
0.993      29.8      18.463
```

```
        1
        2         1
KBR    REPLACED BY CABR2;S
P.V.:201.0;  1 MINUS K  AG
   V.....     D.....     R.
   102.48        5.0
        0          1
      0.0        1.0
0.000      29.8      0.267
0.000      29.8      1.161
0.000      29.8      2.061
0.000      29.8      2.960
0.000      29.8      3.863
0.000      29.8      4.768
0.000      29.8      5.672
0.000      29.8      6.591
0.000      29.8      7.508
0.054      29.8      8.444
0.271      29.8      9.391
0.340      29.8      9.865
0.442      29.8      10.340
0.553      29.8      10.817
0.639      29.8      11.312
0.718      29.8      11.817
0.805      29.8      12.323
0.903      29.8      13.336
0.924      29.8      14.217
0.930      29.8      14.867
0.927      29.8      15.365
0.946      29.8      15.864
0.943      29.8      16.368
0.958      29.8      16.884
0.962      29.8      17.407
0.961      29.8      17.935
0.968      29.8      18.463
```

Experiment 13: Calcium and Potassium

```
        1
        2         1        2        30        18        0       1
KBR    REPLACED BY CABR2;SOIL: 2 LAYER PREII-SAND;FR 500-840; THETA:.317
P.V.:191.4;  CA          AGAINST P.V.
   V.....     D.....     R.....     TO....     rx1...     rx2...
   140.20        5.0          5   13.837          0          0
        0          1          1        0          0          0
      0.0        1.0
0.010      29.7       .193
0.009      29.7      1.159
0.009      29.7      2.119
0.008      29.7      3.083
0.000      29.7      4.059
0.008      29.7      5.036
0.007      29.7      6.020
0.007      29.7      7.013
0.044      29.7      8.021
0.208      29.7      8.513
0.465      29.7      9.015
0.671      29.7      9.516
0.810      29.7      10.018
0.872      29.7      10.591
0.936      29.7      11.016
0.958      29.7      12.004
0.958      29.7      13.011
0.983      29.7      14.042
```

```
        1
        2         1
KBR    REPLACED BY CABR2;S
P.V.:191.4;  1-k        AG
   V.....     D.....     R.
   140.20        5.0
        0          1
      0.0        1.0
0.001      29.7      0.193
0.005      29.7      1.159
0.028      29.7      2.119
0.027      29.7      3.083
0.019      29.7      4.059
0.027      29.7      5.036
0.032      29.7      6.020
0.030      29.7      7.013
0.062      29.7      8.021
0.215      29.7      8.513
0.467      29.7      9.015
0.673      29.7      9.516
0.787      29.7      10.018
0.858      29.7      10.591
0.916      29.7      11.016
0.945      29.7      12.004
0.961      29.7      13.011
0.968      29.7      14.042
```

Experiment 21: Calcium, Sodium, Bromide, and Chloride

```
          1
          2            1          2          30
CABR2 DISPLACED BY NACL; short column nu
P.V.:167.1; 1-ca            AGAINST P.V.
     V.....       D.....    R.....      TO....
    100.20          5.0      2.248       1.416
          0           1          1           0
        0.0         1.0
0.000        14.8       0.118
0.043        14.8       0.471
0.192        14.8       0.824
0.289        14.8       1.060
0.316        14.8       1.178
0.356        14.8       1.297
0.392        14.8       1.416
0.484        14.8       1.774
0.503        14.8       1.894
0.500        14.8       2.013
0.486        14.8       2.132
0.379        14.8       2.491
0.260        14.8       2.611
0.211        14.8       3.091
0.184        14.8       3.331
0.130        14.8       3.689
0.107        14.8       4.283
0.141        14.8       4.877
0.122        14.8       5.478
0.086        14.8       5.598
0.049        14.8       5.717
0.044        14.8       5.837
0.033        14.8       6.074
0.000        14.8       7.248
0.000        14.8       8.431
```

```
          1
          2            1
CABR2 DISPLACED BY NACL;P
P.V.:167.1; NA            A
     V.....       D.....  R.
    100.20          5.0   1.
          0           1
        0.0         1.0
0.01         14.8       0.118
0.14         14.8       0.471
0.28         14.8       0.824
0.40         14.8       1.060
0.41         14.8       1.178
0.41         14.8       1.297
0.54         14.8       1.416
0.61         14.8       1.774
0.62         14.8       1.894
0.58         14.8       2.013
0.58         14.8       2.132
0.46         14.8       2.491
0.34         14.8       2.611
0.29         14.8       3.091
0.28         14.8       3.331
0.24         14.8       3.689
0.22         14.8       4.283
0.17         14.8       4.877
0.16         14.8       5.478
0.15         14.8       5.598
0.12         14.8       5.717
0.12         14.8       5.837
0.12         14.8       6.074
0.02         14.8       7.248
0.01         14.8       8.431
0.00         14.8       10.688
```

```
          1
          2            1
P.V.:167.1; 1-BR          A
calculated with CXTFIT pa
     V.....       D.....  R
    100.20       1326.5   2
          0           0
        0.0         1.0
0.000        14.80      0.118
0.072        14.80      0.471
0.230        14.80      0.706
0.357        14.80      0.943
0.424        14.80      1.178
0.489        14.80      1.298
0.556        14.80      1.416
0.630        14.80      1.655
0.615        14.80      1.755
0.515        14.80      1.894
0.414        14.80      2.013
0.369        14.80      2.133
0.284        14.80      2.250
0.241        14.80      2.371
0.178        14.80      2.611
0.174        14.80      2.850
0.151        14.80      3.091
0.146        14.80      3.331
0.085        14.80      3.689
0.025        14.80      4.283
0.004        14.80      4.878
0.000        14.80      5.478
0.000        14.80      5.718
0.000        14.80      5.957
0.000        14.80      7.248
0.000        14.80      8.432
0.000        14.80      10.689
```

```
          1
          2            1
P.V.:167.1; CL            A
calculating with CXTFIT p
     V.....       D.....  R
    100.20       543.75
          0           0
        0.0         1.0
0.001        14.80      0.118
0.149        14.80      0.471
0.343        14.80      0.706
0.460        14.80      0.942
0.597        14.80      1.178
0.640        14.80      1.298
0.691        14.80      1.416
0.686        14.80      1.656
0.715        14.80      1.775
0.608        14.80      1.894
0.509        14.80      2.013
0.518        14.80      2.133
0.400        14.80      2.25
0.360        14.80      2.371
0.279        14.80      2.611
0.241        14.80      2.853
0.250        14.80      3.091
0.241        14.80      3.331
0.118        14.80      4.283
0.000        14.80      4.877
0.000        14.80      5.718
0.000        14.80      5.957
0.000        14.80      7.248
0.000        14.80      8.432
0.000        14.80      10.689
```

Experiment 22: Calcium, Sodium, Bromide, and Chloride

```
          1
          2            1          2          30
CABR2 DISPLACED BY NACL; short column 2
P.V.:151.3; 1-ca            AGAINST P.V.
     V.....       D.....    R.....      TO....
    100.00          5.0     1.7240       1.376
          0           1          1           0
        0.0         1.0
0.008        15.46      0.335
0.006        15.46      0.558
0.006        15.46      0.781
0.006        15.46      1.004
0.188        15.46      1.228
0.440        15.46      1.454
0.558        15.46      1.681
0.654        15.46      1.907
0.713        15.46      2.133
0.754        15.46      2.358
0.781        15.46      2.470
0.802        15.46      2.581
0.813        15.46      2.693
0.759        15.46      2.805
0.537        15.46      3.029
0.284        15.46      3.252
0.047        15.46      3.477
0.022        15.46      3.704
0.020        15.46      3.931
0.010        15.46      4.158
0.011        15.46      4.385
0.015        15.46      4.834
0.010        15.46      5.945
0.013        15.46      7.044
0.014        15.46      8.167
0.000        15.46      9.297
0.004        15.46      10.424
0.011        15.46      11.554
```

```
          1
          2            1
CABR2 DISPLACED BY NACL;sh
P.V.:151.3; NA            AG
     V.....       D.....  R.
    100.00          5.0   1
          0           1
        0.0         1.0
0.0          15.46      0.335
0.005        15.46      0.558
0.005        15.46      0.781
0.13         15.46      1.004
0.41         15.46      1.228
0.57         15.46      1.454
0.73         15.46      1.681
0.77         15.46      1.907
0.87         15.46      2.133
0.91         15.46      2.358
0.86         15.46      2.470
0.84         15.46      2.581
0.78         15.46      2.693
0.72         15.46      2.805
0.48         15.46      3.029
0.32         15.46      3.252
0.10         15.46      3.477
0.05         15.46      3.704
0.03         15.46      3.931
0.03         15.46      4.158
0.02         15.46      4.385
0.01         15.46      4.834
0.00         15.46      5.945
0.00         15.46      7.044
0.00         15.46      8.167
0.00         15.46      9.297
0.00         15.46      10.424
0.00         15.46      11.554
```

```
          1
          2            1
P.V.:151.3; 1-BR          A

     V.....       D.....  R.
    100.00          1.0   1.
          0           1
        0.0         1.0
0.023        15.46      0.558
0.027        15.46      0.781
0.030        15.46      0.892
0.043        15.46      1.004
0.335        15.46      1.228
0.568        15.46      1.341
0.725        15.46      1.454
0.872        15.46      1.567
0.944        15.46      1.681
1.000        15.46      1.794
1.000        15.46      1.907
1.000        15.46      2.020
1.000        15.46      2.133
0.606        15.46      2.470
0.447        15.46      2.581
0.354        15.46      2.693
0.244        15.46      2.805
0.241        15.46      2.917
0.149        15.46      3.029
0.097        15.46      3.141
0.090        15.46      3.252
0.038        15.46      3.477
0.026        15.46      3.704
0.057        15.46      4.158
0.000        15.46      4.609
0.023        15.46      5.945
0.013        15.46      7.044
0.002        15.46      9.972
```

```
          1
          2            1
P.V.:151.3; CL            A

     V.....       D.....  R
    100.00          1.0
          0           1
        0.0         1.0
0.000        15.46      0.558
0.000        15.46      0.781
0.000        15.46      0.892
0.067        15.46      1.004
0.409        15.46      1.228
0.575        15.46      1.341
0.777        15.46      1.454
0.910        15.46      1.567
1.000        15.46      1.681
0.923        15.46      1.794
0.978        15.46      1.907
0.958        15.46      2.020
0.963        15.46      2.133
0.601        15.46      2.470
0.416        15.46      2.581
0.314        15.46      2.693
0.183        15.46      2.805
0.073        15.46      2.917
0.055        15.46      3.029
0.050        15.46      3.141
0.000        15.46      3.252
0.000        15.46      3.477
0.000        15.46      3.704
0.000        15.46      4.158
0.000        15.46      4.609
0.000        15.46      5.945
0.000        15.46      7.044
0.000        15.46      9.972
```

Experiment 23: Calcium, Sodium, Bromide, and Chloride

```
     1
     2            1           2           30
CABR2 DISPLACED BY NACL;PULSE:300 MIN;SOI
P.V.:132.3; 1 MINUS CA  AGAINST P.V.
    V.....      D.....     R.....      TO....
   128.14          5.0    3.6650       1.760
         0           1         1           0
       0.0         1.0
0.0        15.1      0.147
0.0        15.1      0.880
0.06       15.1      1.613
0.269      15.1      2.348
0.466      15.1      2.789
0.548      15.1      3.082
0.584      15.1      3.228
0.651      15.1      3.520
0.696      15.1      3.813
0.726      15.1      4.105
0.640      15.1      4.542
0.513      15.1      4.688
0.267      15.1      4.980
0.118      15.1      5.271
0.034      15.1      5.999
0.006      15.1      6.729
0.011      15.1      7.461
0.013      15.1      8.943
0.005      15.1      10.449
0.007      15.1      11.946
0.009      15.1      13.394
0.011      15.1      14.880
0.006      15.1      16.374
```

```
     1
     2          1
CABR2 DISPLACED BY NACL;F
P.V.:132.3; NA          A
    V.....     D.....   R
   128.10        5.0
         0         1
       0.0       1.0
0.0        15.1      0.147
0.0        15.1      0.880
0.01       15.1      1.613
0.01       15.1      1.760
0.04       15.1      1.907
0.14       15.1      2.054
0.27       15.1      2.348
0.59       15.1      2.789
0.70       15.1      3.082
0.70       15.1      3.228
0.72       15.1      3.520
0.73       15.1      3.813
0.69       15.1      4.105
0.62       15.1      4.252
0.56       15.1      4.542
0.36       15.1      4.688
0.30       15.1      4.980
0.19       15.1      5.271
0.08       15.1      5.999
0.06       15.1      6.729
0.04       15.1      7.461
0.03       15.1      8.943
0.02       15.1      10.449
0.0        15.1      11.946
0.0        15.1      13.394
0.0        15.1      14.880
0.0        15.1      16.374
```

```
          1
          2          1
P.V.:132.3;   1-BR        AGA

    V.....       D.....    R..
   128.10          1.0     1.
         0           1
       0.0         1.0
0.000      15.1       0.147
0.000      15.1       1.173
0.002      15.1       1.320
0.532      15.1       1.613
0.806      15.1       1.760
0.926      15.1       1.907
0.968      15.1       2.054
1.000      15.1       2.201
1.000      15.1       2.348
1.000      15.1       2.495
1.000      15.1       2.642
1.000      15.1       2.789
0.567      15.1       3.228
0.243      15.1       3.520
0.120      15.1       3.813
0.159      15.1       4.105
0.134      15.1       4.251
0.096      15.1       4.688
0.111      15.1       4.980
0.091      15.1       5.271
0.061      15.1       5.999
0.033      15.1       7.461
0.026      15.1       10.499
0.000      15.1       13.096
0.052      15.1       14.434
```

```
          1
          2          1
P.V.:132.3;   CL          A

    V.....       D.....    R.
   128.10          1.0     1
         0           1
       0.0         1.0
0.000      15.1       0.147
0.000      15.1       1.173
0.000      15.1       1.320
0.501      15.1       1.613
0.730      15.1       1.760
0.873      15.1       1.907
1.000      15.1       2.054
0.972      15.1       2.201
0.933      15.1       2.348
0.902      15.1       2.495
0.876      15.1       2.642
0.895      15.1       2.789
0.406      15.1       3.228
0.223      15.1       3.520
0.148      15.1       3.813
0.087      15.1       4.105
0.000      15.1       4.980
0.000      15.1       5.271
0.000      15.1       5.999
0.000      15.1       7.461
0.000      15.1       10.499
0.000      15.1       13.096
0.000      15.1       14.434
```

Experiment 24: Calcium, Sodium, Bromide, and Chloride

```
     1
     2            1           2           30
CABR2 DISPLACED BY NACL;short column 4
P.V.:128.4; 1 MINUS CA  AGAINST P.V.
    V.....      D.....     R.....      TO....
   116.50          5.0     3.051       1.584
         0           1         1           0
       0.0         1.0
0.018      15.27     0.132
0.018      15.27     0.791
0.018      15.27     1.394
0.066      15.27     1.717
0.210      15.27     2.114
0.355      15.27     2.511
0.489      15.27     2.909
0.562      15.27     3.174
0.617      15.27     3.440
0.618      15.27     3.705
0.451      15.27     4.102
0.402      15.27     4.233
0.332      15.27     4.496
0.265      15.27     4.759
0.172      14.27     5.418
0.093      15.27     6.082
0.036      15.27     6.741
0.024      15.27     8.089
0.017      15.27     9.430
0.012      15.27     10.756
0.004      15.27     12.082
0.000      15.27     13.409
0.004      15.27     14.749
```

```
     1
     2          1
CABR2 DISPLACED BY NACL;s
P.V.:128.4;  NA         A
    V.....     D.....   R.
   116.50        5.0    2.
         0         1
       0.0       1.0
0.000      15.27     0.132
0.000      15.27     0.791
0.040      15.27     1.394
0.130      15.27     1.717
0.330      15.27     2.114
0.440      15.27     2.511
0.540      15.27     2.909
0.630      15.27     3.174
0.660      15.27     3.440
0.650      15.27     3.573
0.650      15.27     3.705
0.630      15.27     3.873
0.480      15.27     4.102
0.440      15.27     4.233
0.350      15.27     4.496
0.290      15.27     4.759
0.280      15.27     5.418
0.140      15.27     6.082
0.100      15.27     6.741
0.050      15.27     8.089
0.040      15.27     9.430
0.020      15.27     11.802
0.010      15.27     14.454
```

```
          1
          2          1
P.V.:128.4;   1-BR        AG

    V.....       D.....    R.
   116.50          1.0     1
         0           1
       0.0         1.0
0.000      15.27      0.132
0.000      15.27      0.791
0.449      15.27      1.394
0.895      15.27      1.717
0.793      15.27      1.849
0.880      15.27      1.982
0.940      15.27      2.114
0.967      15.27      2.247
0.960      15.27      2.379
0.848      15.27      2.511
0.556      15.27      2.777
0.422      15.27      2.909
0.366      15.27      3.042
0.283      15.27      3.174
0.178      15.27      3.307
0.156      15.27      3.572
0.047      15.27      3.837
0.070      15.27      4.102
0.004      15.27      4.365
0.083      15.27      4.496
0.023      15.27      5.418
0.055      15.27      6.741
0.051      15.27      8.089
0.000      15.27      9.430
```

```
          1
          2          1
P.V.:128.4;   CL          AG

    V.....       D.....    R.
   116.50          1.0     1
         0           1
       0.0         1.0
0.000      15.27      0.132
0.000      15.27      0.791
0.591      15.27      1.394
0.704      15.27      1.717
0.878      15.27      1.849
0.872      15.27      1.982
1.000      15.27      2.114
0.943      15.27      2.247
0.995      15.27      2.379
0.910      15.27      2.511
0.668      15.27      2.777
0.575      15.27      2.909
0.475      15.27      3.042
0.407      15.27      3.174
0.361      15.27      3.307
0.214      15.27      3.572
0.118      15.27      3.837
0.074      15.27      4.102
0.045      15.27      4.365
0.043      15.27      4.496
0.000      15.27      5.418
0.000      15.27      6.741
0.000      15.27      8.089
0.000      15.27      9.430
```

Experiment 25: Calcium, Sodium, Bromide, and Chloride

```
    1
    2          1          2          30
CABR2 DISPLACED BY NACL;PULSE:300 MIN,sho
P.V.: 93.0; 1 - ca      AGAINST P.V.
   V.....     D.....     R.....     TO....
  146.02        5.0     1.261      3.411
     0           1          1          0
    0.0       1.0
0.002     14.8     0.117
0.000     14.8     0.354
0.005     14.8     0.531
0.007     14.8     0.708
0.083     14.8     0.885
0.562     14.8     1.062
0.851     14.8     1.239
0.928     14.8     1.416
0.966     14.8     1.711
0.971     14.8     1.881
0.984     14.8     2.561
0.991     14.8     3.411
0.992     14.8     3.580
0.993     14.8     4.086
0.972     14.8     4.255
0.526     14.8     4.424
0.184     14.8     4.593
0.098     14.8     4.761
0.055     14.8     5.272
0.054     14.8     5.447
0.046     14.8     6.139
0.037     14.8     7.000
0.025     14.8     8.679
0.038     14.8     10.360
0.036     14.8     12.035
0.032     14.8     13.787
0.026     14.8     15.549
0.023     14.8     17.306
0.026     14.8     19.019
```

```
      1
      2          1
CABR2 DISPLACED BY NACL;P
P.V.: 93.0; na           A
   V.....     D.....     R
  146.02        5.0
     0           1
    0.0       1.0
0.00      14.8     0.117
0.00      14.8     0.354
0.00      14.8     0.531
0.07      14.8     0.708
0.08      14.8     0.885
0.55      14.8     1.062
0.87      14.8     1.239
0.94      14.8     1.416
0.94      14.8     1.711
0.94      14.8     1.881
0.97      14.8     2.561
0.98      14.8     3.411
1.00      14.8     3.580
0.94      14.8     4.086
0.46      14.8     4.255
0.16      14.8     4.424
0.06      14.8     4.593
0.01      14.8     4.761
0.01      14.8     5.272
0.00      14.8     5.447
0.00      14.8     6.139
0.00      14.8     7.000
0.00      14.8     8.679
0.00      14.8     10.360
0.00      14.8     12.035
0.00      14.8     13.787
0.00      14.8     15.549
0.00      14.8     17.306
0.00      14.8     19.019
```

```
      1
      2          1
CABR2 DISPLACED BY NACL;Pl
P.V.: 93.0; 1-br
   V.....     D.....     R.
  146.02        5.0      1
     0           1
    0.0       1.0
0.00      14.8     0.354
0.024     14.8     0.708
0.048     14.8     0.885
0.621     14.8     1.062
0.908     14.8     1.239
1.000     14.8     1.416
1.000     14.8     1.711
1.000     14.8     1.881
1.000     14.8     2.051
1.000     14.8     2.391
1.000     14.8     2.731
1.000     14.8     3.071
1.000     14.8     3.411
1.000     14.8     3.749
1.000     14.8     4.086
0.879     14.8     4.255
0.309     14.8     4.424
0.130     14.8     4.593
0.054     14.8     4.761
0.019     14.8     5.099
0.020     14.8     5.447
0.016     14.8     5.792
0.000     14.8     7.504
0.005     14.8     9.184
0.0       14.8     10.860
0.0       14.8     12.560
```

```
      1
      2          1
CABR2 DISPLACED BY NACL;Pl
P.V.: 93.0; cl           A(
   V.....     D.....     R.
  146.02        5.0
     0           1
    0.0       1.0
0.00      14.8     0.354
0.035     14.8     0.708
0.068     14.8     0.885
0.620     14.8     1.062
0.883     14.8     1.239
0.973     14.8     1.416
0.911     14.8     1.711
0.896     14.8     1.881
0.928     14.8     2.051
0.955     14.8     2.391
0.908     14.8     2.731
1.000     14.8     3.071
0.979     14.8     3.411
0.987     14.8     3.749
0.993     14.8     4.086
0.843     14.8     4.255
0.356     14.8     4.424
0.100     14.8     4.593
0.039     14.8     4.761
0.023     14.8     5.099
0.000     14.8     5.447
0.074     14.8     5.792
0.043     14.8     7.504
0.0       14.8     9.184
0.0       14.8     10.860
0.0       14.8     12.560
```

Experiment 26: Calcium, Sodium, Bromide, and Chloride

```
    1
    2          1          2          30
CABR2 DISPLACED BY NACL;short column 2
P.V.:154.0; 1-ca        AGAINST P.V.
   V.....     D.....     R.....     TO....
   74.12        5.0     2.958      1.665
     0           1          1          0
    0.0       1.0
0.000     15.46    0.083
0.001     15.46    0.916
0.008     15.46    1.249
0.168     15.46    1.748
0.194     15.46    1.831
0.210     15.46    1.998
0.350     15.46    2.164
0.421     15.46    2.331
0.500     15.46    2.580
0.501     15.46    2.664
0.544     15.46    2.830
0.567     15.46    2.996
0.608     15.46    3.163
0.706     15.46    3.413
0.712     15.46    3.496
0.722     15.46    3.662
0.695     15.46    3.829
0.614     15.46    3.995
0.517     15.46    4.245
0.472     15.46    4.328
0.420     15.46    4.495
0.376     15.46    4.661
0.316     15.46    4.828
0.179     15.46    5.077
0.035     15.46    5.910
0.032     15.46    6.742
0.018     15.46    7.574
0.017     15.46    8.407
0.017     15.46    9.239
```

```
      1
      2          1
CABR2 DISPLACED BY NACL;sh
P.V.:154.0; NA          AG
   V.....     D.....     R.
   74.12        5.0      2
     0           1
    0.0       1.0
0.00      15.46    0.083
0.00      15.46    0.916
0.06      15.46    1.249
0.27      15.46    1.748
0.30      15.46    1.831
0.37      15.46    1.998
0.45      15.46    2.164
0.53      15.46    2.331
0.63      15.46    2.580
0.64      15.46    2.664
0.66      15.46    2.830
0.67      15.46    2.996
0.69      15.46    3.163
0.66      15.46    3.413
0.63      15.46    3.496
0.61      15.46    3.662
0.60      15.46    3.829
0.47      15.46    3.995
0.38      15.46    4.245
0.36      15.46    4.328
0.34      15.46    4.495
0.31      15.46    4.661
0.27      15.46    4.828
0.16      15.46    5.077
0.02      15.46    5.910
0.00      15.46    6.742
0.00      15.46    7.574
0.00      15.46    8.407
0.00      15.46    9.239
```

```
      1
      2          1
CABR2 DISPLACED BY NACL;sl
P.V.:154.0; 1-br         Al
   V.....     D.....     R
   74.12        5.0
     0           1
    0.0       1.0
0.018     15.46    0.083
0.000     15.46    0.916
0.188     15.46    1.249
0.836     15.46    1.748
1.000     15.46    1.831
1.000     15.46    2.164
0.920     15.46    2.580
0.834     15.46    2.664
0.657     15.46    2.830
0.533     15.46    2.996
0.274     15.46    3.163
0.151     15.46    3.413
0.153     15.46    3.662
0.119     15.46    3.829
0.112     15.46    3.995
0.072     15.46    4.328
0.021     15.46    4.495
0.000     15.46    5.910
0.000     15.46    7.574
```

```
      1
      2          1
CABR2 DISPLACED BY NACL;s
P.V.:154.0; cl           A
   V.....     D.....     R
   74.12        5.0
     0           1
    0.0       1.0
0.000     15.46    0.083
0.000     15.46    0.916
0.252     15.46    1.249
0.762     15.46    1.748
0.928     15.46    1.831
1.000     15.46    1.998
0.956     15.46    2.164
0.963     15.46    2.331
0.860     15.46    2.580
0.818     15.46    2.664
0.630     15.46    2.830
0.505     15.46    2.996
0.291     15.46    3.163
0.037     15.46    3.413
0.008     15.46    3.496
0.000     15.46    3.662
0.000     15.46    3.829
0.000     15.46    3.995
0.000     15.46    4.245
0.000     15.46    4.328
```

Experiment 27: Calcium, Sodium, Bromide, and Chloride

```
    1
    2        1          2          30
CABR2 DISPLACED BY NACL
P.V.:156.2; 1-ca        AGAINST P.V.
   V.....    D.....     R.....     TO....
  91.51         5.0     3.201      2.080
      0           1         1          0
    0.0         1.0
0.000     15.1      0.104
0.053     15.1      1.141
0.037     15.1      2.184
0.243     15.1      2.497
0.406     15.1      2.810
0.468     15.1      3.263
0.607     15.1      3.539
0.649     15.1      3.852
0.692     15.1      4.270
0.716     15.1      4.585
0.733     15.1      4.900
0.678     15.1      5.321
0.554     15.1      5.636
0.204     15.1      5.951
0.027     15.1      6.371
0.012     15.1      8.585
0.000     15.1      9.658
0.008     15.1      9.732
0.004     15.1      10.781
```

```
       1
       2         1
CABR2 DISPLACED BY NACL
P.V.:156.2; NA          AG
    V.....     D.....   R.
   91.51         5.0    3
       0           1
     0.0         1.0
0.00        15.1        0.104
0.00        15.1        1.141
0.14        15.1        2.184
0.34        15.1        2.497
0.40        15.1        2.810
0.54        15.1        3.263
0.53        15.1        3.539
0.60        15.1        3.852
0.64        15.1        4.270
0.65        15.1        4.585
0.64        15.1        4.900
0.62        15.1        5.321
0.45        15.1        5.636
0.18        15.1        5.951
0.03        15.1        6.371
0.00        15.1        8.585
0.00        15.1        9.658
0.00        15.1        9.732
0.00        15.1        10.781
```

```
       1
       2         1
CABR2 DISPLACED BY NACL;P
P.V.:156.2; br          A
   V.....     D.....    R
  91.51         5.0
      0           1
    0.0         1.0
0.027     15.1      0.830
0.109     15.1      1.037
0.246     15.1      1.141
0.886     15.1      1.350
1.000     15.1      1.558
1.000     15.1      1.663
1.000     15.1      1.767
1.000     15.1      1.871
1.000     15.1      1.975
1.000     15.1      2.080
1.000     15.1      2.184
1.000     15.1      2.288
1.000     15.1      2.392
1.000     15.1      2.601
1.000     15.1      2.705
1.000     15.1      2.810
0.901     15.1      2.914
0.888     15.1      3.018
0.769     15.1      3.122
0.101     15.1      3.331
0.000     15.1      3.539
0.028     15.1      3.750
0.044     15.1      3.956
0.070     15.1      4.585
0.013     15.1      5.636
0.004     15.1      6.685
```

```
       1
       2         1
CABR2 DISPLACED BY NACL;P
P.V.:156.2; cl          A
   V.....     D.....    R
  91.51         5.0
      0           1
    0.0         1.0
0.000     15.1      0.519
0.000     15.1      0.830
0.091     15.1      1.037
0.169     15.1      1.141
0.758     15.1      1.350
0.945     15.1      1.558
0.951     15.1      1.663
0.987     15.1      1.767
0.954     15.1      1.871
0.953     15.1      1.975
1.000     15.1      2.080
0.961     15.1      2.184
0.966     15.1      2.288
0.953     15.1      2.392
0.917     15.1      2.601
0.914     15.1      2.705
0.908     15.1      2.810
0.804     15.1      2.914
0.815     15.1      3.018
0.707     15.1      3.122
0.158     15.1      3.331
0.000     15.1      3.539
0.000     15.1      3.750
0.000     15.1      3.956
0.000     15.1      4.585
0.000     15.1      5.636
0.000     15.1      6.685
0.000     15.1      7.838
```

Experiment 28: Calcium, Sodium, Bromide, and Chloride

```
     1
     2         1          2         30
CABR2 DISPLACED BY NACL;short column 4
P.V.:130.1;  1-ca       AGAINST P.V.
   V.....    D.....     R.....    TO....
  118.76        5.0       2.13     2.595
       0          1          1         0
     0.0        1.0
0.001     15.27     0.135
0.000     15.27     0.540
0.006     15.27     0.946
0.102     15.27     1.351
0.211     15.27     1.485
0.317     15.27     1.620
0.460     15.27     1.754
0.491     15.27     1.889
0.548     15.27     2.023
0.591     15.27     2.157
0.657     15.27     2.292
0.706     15.27     2.595
0.723     15.27     2.722
0.768     15.27     3.103
0.798     15.27     3.495
0.834     15.27     3.866
0.861     15.27     4.104
0.842     15.27     4.141
0.848     15.27     4.279
0.712     15.27     4.416
0.577     15.27     4.692
0.437     15.27     4.967
0.140     15.27     5.378
0.036     15.27     6.736
0.001     15.27     8.117
```

```
       1
       2         1
CABR2 DISPLACED BY NACL;s
P.V.:130.1;  na         A
   V.....     D.....    R
  118.76        5.0
       0          1
     0.0        1.0
0.00        15.27       0.135
0.00        15.27       0.540
0.00        15.27       0.946
0.17        15.27       1.351
0.26        15.27       1.485
0.34        15.27       1.620
0.40        15.27       1.754
0.47        15.27       1.889
0.52        15.27       2.023
0.57        15.27       2.157
0.63        15.27       2.292
0.74        15.27       2.595
0.74        15.27       2.722
0.80        15.27       3.103
0.82        15.27       3.495
0.82        15.27       3.866
0.85        15.27       4.104
0.77        15.27       4.141
0.82        15.27       4.279
0.75        15.27       4.416
0.65        15.27       4.692
0.37        15.27       4.967
0.13        15.27       5.378
0.00        15.27       6.736
0.00        15.27       8.117
```

```
       1
       2         1
CABR2 DISPLACED BY NACL;s
P.V.:130.1;, br         A
   V.....     D.....    R.
  118.76        5.0
       0          1
     0.0        1.0
0.000     15.27     0.540
0.295     15.27     0.946
0.561     15.27     1.081
0.934     15.27     1.351
0.949     15.27     1.485
1.000     15.27     1.620
1.000     15.27     1.754
1.000     15.27     1.889
1.000     15.27     2.023
1.000     15.27     2.157
1.000     15.27     2.426
1.000     15.27     2.595
1.000     15.27     2.722
1.000     15.27     2.848
1.000     15.27     2.932
1.000     15.27     3.103
1.000     15.27     3.231
0.914     15.27     3.313
0.586     15.27     3.495
0.320     15.27     3.408
0.130     15.27     3.866
0.127     15.27     4.141
0.075     15.27     4.416
0.034     15.27     4.692
0.012     15.27     5.242
0.000     15.27     7.033
0.004     15.27     9.887
```

```
       1
       2         1
CABR2 DISPLACED BY NACL;s
P.V.:130.1;  cl         A
   V.....     D.....    R.
  118.76        5.0
       0          1
     0.0        1.0
0.000     15.27     0.540
0.033     15.27     0.811
0.261     15.27     0.946
0.597     15.27     1.081
0.891     15.27     1.351
0.952     15.27     1.485
0.969     15.27     1.620
0.991     15.27     1.754
1.000     15.27     1.889
0.997     15.27     2.023
0.958     15.27     2.157
0.958     15.27     2.426
0.968     15.27     2.595
0.953     15.27     2.722
0.918     15.27     2.848
0.913     15.27     2.932
0.919     15.27     3.103
0.913     15.27     3.231
0.793     15.27     3.313
0.529     15.27     3.495
0.266     15.27     3.408
0.066     15.27     3.866
0.0       15.27     4.141
0.0       15.27     4.416
0.0       15.27     4.692
0.0       15.27     5.242
0.0       15.27     5.784
```

Experiment 31: Calcium, Potassium, and Sodium

```
P.V.:167.1; 1-ca        AGAINST P.V.
   V.....     D.....     R.....     TO....
   99.24        5.0      3.141      2.838
       0          1          1          0
     0.0        1.0
0.002     14.80     0.226
0.064     14.80     0.452
0.175     14.80     0.678
0.223     14.80     0.903
0.337     14.80     1.357
0.382     14.80     1.584
0.431     14.80     1.811
0.492     14.80     2.153
0.514     14.80     2.495
0.558     14.80     2.952
0.586     14.80     3.411
0.555     14.80     3.644
0.515     14.80     3.878
0.472     14.80     4.111
0.389     14.80     4.345
0.297     14.80     4.578
0.254     14.80     4.811
0.223     14.80     5.045
0.204     14.80     5.278
0.186     14.80     5.512
0.177     14.80     5.745
0.166     14.80     5.978
0.160     14.80     6.211
0.149     14.80     6.443
0.131     14.80     6.910
0.129     14.80     7.370
0.128     14.80     7.838
0.110     14.80     8.537
0.093     14.80     9.236
0.049     14.80     10.524
0.036     14.80     11.699
0.017     14.80     12.892
0.004     14.80     13.964
```

```
P.V.:167.1  K
   V.....     D.....     R.....     TO....
   99.28        5.0      5.139      2.838
       0          1          1          0
     0.0        1.0
0.002     14.80     0.226
0.004     14.80     0.452
0.002     14.80     0.678
0.004     14.80     0.904
0.042     14.80     1.357
0.070     14.80     1.584
0.104     14.80     1.811
0.198     14.80     2.153
0.238     14.80     2.495
0.302     14.80     2.952
0.440     14.80     3.411
0.590     14.80     3.644
0.586     14.80     3.878
0.556     14.80     4.111
0.486     14.80     4.345
0.380     14.80     4.578
0.324     14.80     4.811
0.296     14.80     5.045
0.278     14.80     5.278
0.272     14.80     5.512
0.270     14.80     5.745
0.272     14.80     5.978
0.270     14.80     6.211
0.260     14.80     6.443
0.232     14.80     6.910
0.214     14.80     7.370
0.172     14.80     7.838
0.158     14.80     8.537
0.120     14.80     9.236
0.078     14.80     10.524
0.058     14.80     11.699
0.048     14.80     12.892
0.042     14.80     13.964
```

```
                  1
                  2          1          2          0
CABR2 DISPLACED BY NACL AND KCL, short c
P.V.:167.1; NA                AGAINST P.V.   C
   V.....     D.....     R.....     TO....
   99.24     840.46      1.642      2.838
       0          0          0          0
     0.0        1.0
0.0156    14.80     0.226
0.1716    14.80     0.452
0.390     14.80     0.678
0.4524    14.80     0.904
0.5304    14.80     1.130
0.6084    14.80     1.357
0.702     14.80     1.584
0.7176    14.80     1.811
0.7488    14.80     2.038
0.7488    14.80     2.266
0.7976    14.80     2.495
0.8112    14.80     2.723
0.8268    14.80     2.952
0.7956    14.80     3.182
0.6864    14.80     3.411
0.4992    14.80     3.644
0.4524    14.80     3.878
0.390     14.80     4.111
0.3278    14.80     4.345
0.2496    14.80     4.578
0.1560    14.80     5.161
0.1248    14.80     5.512
0.0936    14.80     5.978
0.078     14.80     6.443
0.0624    14.80     6.910
0.0312    14.80     8.537
0.0156    14.80     9.236
0.0       14.80     10.524
0.0       14.80     11.699
0.0       14.80     12.892
0.0       14.80     13.964
```

Experiment 32: Calcium, Potassium, and Sodium

```
P.V.:151.3; CA          AGAINST P.V.
   V.....     D.....     R.....     TO....
   98.25        5.0      2.560      2.699
       0          1          1          0
     0.0        1.0
0.005     15.40     0.214
0.014     15.40     0.429
0.037     15.40     0.858
0.114     15.40     1.072
0.194     15.40     1.288
0.350     15.40     1.504
0.422     15.40     1.719
0.444     15.40     1.935
0.456     15.40     2.151
0.477     15.40     2.589
0.495     15.40     2.808
0.515     15.40     3.027
0.531     15.40     3.246
0.546     15.40     3.468
0.552     15.40     3.692
0.567     15.40     3.914
0.474     15.40     4.137
0.298     15.40     4.360
0.317     15.40     4.583
0.409     15.40     4.807
0.481     15.40     5.030
0.529     15.40     5.254
0.550     15.40     5.477
0.563     15.40     5.700
0.549     15.40     5.924
0.459     15.40     6.147
0.346     15.40     6.371
0.246     15.40     6.594
0.086     15.40     7.041
0.048     15.40     7.488
0.020     15.40     7.932
0.000     15.40     8.824
0.000     15.40     10.052
0.000     15.40     11.178
0.000     15.40     12.370
0.000     15.40     13.370
```

```
                  1
                  2          1          2          30
CABR2 DISPLACED BY NACL AND KCL
P.V.:151.3; NA                AGAINST P.V.
   V.....     D.....     R.....     TO....
   98.25        5.0      2.411      2.699
       0          1          1          0
     0.0        1.0
0.02      15.40     0.214
0.07      15.40     0.429
0.11      15.40     0.858
0.32      15.40     1.072
0.58      15.40     1.288
0.81      15.40     1.504
0.95      15.40     1.719
0.93      15.40     1.935
0.95      15.40     2.151
0.98      15.40     2.370
1.00      15.40     2.589
0.98      15.40     2.808
0.96      15.40     3.027
0.96      15.40     3.246
0.96      15.40     3.468
0.91      15.40     3.692
0.74      15.40     3.914
0.42      15.40     4.137
0.12      15.40     4.360
0.05      15.40     4.807
0.04      15.40     5.477
0.04      15.40     7.488
0.03      15.40     10.052
0.03      15.40     11.178
0.02      15.40     12.370
0.01      15.40     13.370
```

```
P.V.:151.3; K                 AGAINST P.V.
   V.....     D.....     R.....     TO....
   98.25      53.50      4.419      2.699
       0          0          0          0
     0.0        1.0
0.002     15.40     0.214
0.002     15.40     0.429
0.002     15.40     0.858
0.002     15.40     1.072
0.002     15.40     1.288
0.002     15.40     1.504
0.002     15.40     1.719
0.002     15.40     1.935
0.002     15.40     2.151
0.021     15.40     2.589
0.042     15.40     2.808
0.062     15.40     3.027
0.080     15.40     3.246
0.096     15.40     3.468
0.136     15.40     3.692
0.200     15.40     3.914
0.272     15.40     4.137
0.366     15.40     4.360
0.532     15.40     4.583
0.700     15.40     4.807
0.828     15.40     5.030
0.916     15.40     5.254
0.974     15.40     5.477
1.000     15.40     5.700
0.974     15.40     5.924
0.822     15.40     6.147
0.620     15.40     6.371
0.442     15.40     6.594
0.230     15.40     7.041
0.134     15.40     7.488
0.088     15.40     7.932
0.048     15.40     8.824
0.026     15.40     10.052
0.020     15.40     11.178
0.014     15.40     12.370
0.012     15.40     13.370
```

Experiment 33: Calcium, Potassium, and Sodium

```
      1
      2          1          2         30
CABR2 DISPLACED BY NACL AND KCL
P.V.:145.8; CA             AGAINST P.V.
   V.....      D.....      R.....     TO....
    98.55          5.0      2.542      1.999
        0            1          1          0
      0.0          1.0
0.000       15.10     0.203
0.016       15.10     0.344
0.083       15.10     0.406
0.144       15.10     0.573
0.211       15.10     0.802
0.283       15.10     1.146
0.376       15.10     1.604
0.443       15.10     2.063
0.475       15.10     2.292
0.465       15.10     2.516
0.429       15.10     2.739
0.405       15.10     2.963
0.362       15.10     3.186
0.316       15.10     3.410
0.266       15.10     3.638
0.227       15.10     3.868
0.227       15.10     4.096
0.163       15.10     4.554
0.136       15.10     5.012
0.112       15.10     5.698
0.116       15.10     6.154
0.078       15.10     6.838
0.054       15.10     7.983
0.021       15.10     9.130
0.022       15.10     10.247
0.020       15.10     11.383
```

```
      1
      2          1          2         30
CABR2 DISPLACED BY NACL AND KCL
P.V.:145.8; K              AGAINST P.V.
   V.....      D.....      R.....     TO....
    98.55          5.0       3.88      1.999
        0            1          1          0
      0.0          1.0
0.004       15.10     0.203
0.002       15.10     0.344
0.004       15.10     0.406
0.004       15.10     0.573
0.004       15.10     0.802
0.014       15.10     1.146
0.110       15.10     1.604
0.198       15.10     2.063
0.232       15.10     2.292
0.332       15.10     2.516
0.502       15.10     2.739
0.570       15.10     2.963
0.530       15.10     3.186
0.438       15.10     3.410
0.348       15.10     3.638
0.280       15.10     3.868
0.218       15.10     4.096
0.154       15.10     4.554
0.122       15.10     5.012
0.088       15.10     5.698
0.086       15.10     6.154
0.058       15.10     6.838
0.044       15.10     7.983
0.038       15.10     9.130
0.034       15.10     10.247
0.032       15.10     11.383
```

```
      1
      2          1          2         30
CABR2 DISPLACED BY NACL AND KCL
P.V.:145.8; NA             AGAINST P.V.
   V.....      D.....      R.....     TO....
    98.55        100.0      1.958      1.999
        0            1          1          0
      0.0          1.0
0.02        15.10     0.203
0.10        15.10     0.344
0.24        15.10     0.406
0.34        15.10     0.573
0.48        15.10     0.802
0.68        15.10     1.146
0.76        15.10     1.604
0.72        15.10     2.063
0.62        15.10     2.292
0.38        15.10     2.516
0.28        15.10     2.739
0.24        15.10     2.963
0.22        15.10     3.186
0.20        15.10     3.410
0.20        15.10     3.638
0.20        15.10     3.868
0.18        15.10     4.096
0.08        15.10     4.554
0.04        15.10     5.012
0.02        15.10     5.698
0.02        15.10     6.838
0.02        15.10     7.983
0.02        15.10     9.132
0.02        15.10     10.247
0.00        15.10     11.383
```

Experiment 34: Calcium, Potassium, and Sodium

```
P.V.:138.4; CA             AGAINST P.V.
   V.....      D.....      R.....     TO....
   120.00          5.0      5.907      2.392
        0            1          1          0
      0.0          1.0
0.000       15.30     0.271
0.000       15.30     0.542
0.000       15.30     1.084
0.000       15.30     1.628
0.247       15.30     2.173
0.101       15.30    -1.901
0.347       15.30     2.446
0.407       15.30     2.719
0.455       15.30     3.268
0.522       15.30     3.816
0.423       15.30     4.370
0.135       15.30     4.925
0.533       15.30     4.092
0.052       15.30     5.451
0.021       15.30     6.012
0.017       15.30     6.849
0.000       15.30     7.515
0.028       15.30     7.914
0.060       15.30     8.180
0.101       15.30     8.468
0.128       15.30     8.755
0.145       15.30     9.043
0.159       15.30     9.330
0.147       15.30     9.474
0.155       15.30     10.049
0.177       15.30     10.624
0.149       15.30     11.195
0.138       15.30     11.753
0.134       15.30     12.450
0.118       15.30     12.818
0.106       15.30     13.301
0.090       15.30     14.14
0.083       15.30     14.70
0.072       15.30     15.12
0.054       15.30     15.68
```

```
      1
      2          1          2         30
CABR2 DISPLACED BY NACL AND KCL
P.V.:138.4; NA             AGAINST P.V.
   V.....      D.....      R.....     TO....
   120.00          5.0      2.955      2.392
        0            1          1          0
      0.0          1.0
0.00        15.30     0.271
0.00        15.30     0.542
0.00        15.30     1.084
0.04        15.30     1.628
0.50        15.30     2.173
0.32        15.30     1.901
0.56        15.30     2.446
0.90        15.30     2.719
1.00        15.30     3.268
0.98        15.30     3.816
0.78        15.30     4.370
0.28        15.30     4.925
0.92        15.30     4.092
0.10        15.30     5.451
0.06        15.30     6.012
0.02        15.30     6.849
0.02        15.30     8.180
0.00        15.30     10.049
0.00        15.30     11.195
0.00        15.30     12.818
```

```
P.V.:138.4; K              AGAINST P.V.
   V.....      D.....      R.....     TO....
   120.00          5.0     10.775      2.392
        0            1          1          0
      0.0          1.0
0.002       15.30     0.271
0.002       15.30     0.542
0.002       15.30     1.084
0.002       15.30     1.628
0.004       15.30     2.173
0.004       15.30     1.901
0.004       15.30     2.446
0.004       15.30     2.719
0.004       15.30     3.268
0.004       15.30     3.816
0.004       15.30     4.370
0.002       15.30     4.925
0.004       15.30     4.092
0.002       15.30     5.451
0.002       15.30     6.012
0.002       15.30     6.849
0.002       15.30     7.515
0.002       15.30     7.914
0.104       15.30     8.180
0.200       15.30     8.468
0.254       15.30     8.755
0.282       15.30     9.043
0.298       15.30     9.330
0.324       15.30     9.474
0.348       15.30     10.049
0.302       15.30     10.624
0.272       15.30     11.195
0.238       15.30     11.753
0.216       15.30     12.450
0.188       15.30     12.818
0.164       15.30     13.301
0.142       15.30     14.140
0.124       15.30     14.70
0.114       15.30     15.12
0.098       15.30     15.68
```

APPENDIX E

Exchange Data

Exchange isotherms in a binary system, A/B, were formulated in a previous study *(12)* as:

$$Y_A = \alpha + \beta X_A + \gamma X_A^2 + \delta X_A^3 \qquad \text{(E-1)}$$

where X and Y are the dimensionless concentrations in the liquid and adsorbed phases, respectively. The isotherm for the competing cation B follows from:

$$Y_B = 1-\alpha-\beta-\gamma-\delta + (\beta+2\gamma+3\delta)X_B - (\gamma+3\delta)X_B^2 + \delta X_B^3 \qquad \text{(E-2)}$$

Parameter values for the exchange isotherms and CEC values for the soil systems used in this study are listed below:

Exchange Properties for Ca/Na Soils

Soil	CEC $cmol_c/kg$	Cation	α	β	γ	δ
Dothan I	0.600	Ca	0	2.32	-2.24	0.94
		Na	-0.02	0.66	-0.58	0.94
Dothan II	0.253	Ca	0.02	3.90	-7.05	4.21
		Na	-0.08	2.43	-5.58	4.21
Wickham I	0.697	Ca	0.28	4.01	-7.66	4.43
		Na	-0.06	1.98	-5.63	4.43
Wickham II	0.619	Ca	0.31	4.06	-8.12	4.82
		Na	-0.07	0.18	-6.34	4.82
Troup	0.002	Ca	0.10	0.64	-0.52	0.86
		Na	-0.08	2.18	-2.06	0.86
Lucedale I	0.618	Ca	0.02	6.14	-11.48	6.37
		Na	-0.05	2.29	-7.63	6.37
Lucedale II	0.991	Ca	0.01	3.31	-4.63	2.35
		Na	-0.04	1.10	-2.42	2.35
Savannah I	0.363	Ca	0.16	4.67	-8.79	5.02
		Na	-0.06	2.15	-6.27	5.02