Evaluation of Methods to Determine CEC and Exchange Isotherms for Modeling Transport

EVALUATION OF METHODS TO DETERMINE CEC AND EXCHANGE ISOTHERMS

FOR MODELING TRANSPORT

Feike J. Leij and J.H. Dane

Grauate Student and Professor
of Agronomy and Soils

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ABSTRACT

Knowledge of cationic transport in soils is important from an agricultural and an environmental point of view. To reliably predict transport of cations that react with the soil matrix, it is necessary to know the cation exchange capacity (CEC) and the adsorption isotherms for the cations. This publication presents a two-step displacement method to determine exchange isotherms and discusses several aspects influencing the determination of CEC. CEC values were found to depend on the method of determination (batch or displacement), the saturating cation (Ca, Na or K), and the concentration of the extractant. The two-step method to determine exchange isotherms was relatively fast and yielded a complete curve using only one sample under conditions similar to those during transport. An error analysis indicated that accurate determinations of exchange isotherms could be carried out using this method. All exchange isotherms showed pronounced deviations from linearity. Based on these findings, it is concluded that more attention needs to be directed to the determination of exchange data in order to successfully model solute transport.

INTRODUCTION

Solute transport in soils is influenced by the way in which the solute reacts in and with the soil. Precipitation, dissolution, exchange, exclusion, adsorption, complexation etc. are all reactions which can affect chemical transport. In this report, only the exchange of cations by the soil will be considered. Two different effects of exchange on transport can be distinguished. First, the mean velocity of a reactive solute differs from the mean velocity of the carrier. Cations, which are adsorbed by the negatively charged soil particles, will lag behind the average position of the carrier front. Anions, which are generally excluded, will travel ahead of the carrier front. Second, the nature of the exchange reaction determines the amount of solute spreading (1). These effects of ion exchange, retardation and spreading due to non-linearity of the exchange isotherm, are usually accounted for by including the retardation factor, R, in the transport equation. This factor is defined as follows:

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

where ρ is the bulk density $[ML^{-3}]$, θ is the volumetric water content $[L^3L^{-3}]$, S is the solute concentration in the adsorbed phase $[MM^{-1}]$, and C is the solute concentration in the liquid phase $[ML^{-3}]$.

To solve the transport equation for a particular solute species, the total solute concentration in the adsorbed phase and the relationship between the concentrations in adsorbed and liquid phase needs to be known. This relationship, the exchange isotherm, depends on the type and relative amounts of all the solute species present in the

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adsorbed and liquid phase. For simplicity, however, the exchange isotherm is usually determined in a binary system at a constant electrolyte level.

This investigation assumed instantaneous equilibrium for the exchange reactions and the absence of hysteresis. The values of the selectivity coefficient of these reactions determine the distribution of cations between the solution and adsorbed phase for a particular solute (8). In transport studies, this distribution is quantified with the distribution coefficient, K_d, the slope of the exchange isotherm, which can be written as $\frac{dS}{dC}$ for a binary system with constant electrolyte level. Usually the value of K_d is not constant over the whole range of the exchange isotherm (except for trace amounts of solute or in case of partial exchange), and the exchange isotherm needs to be measured to predict transport. Persaud and Wierenga (12) studied the more general case for $\partial S/\partial C$, which needs to be employed if the restrictive conditions are not met.

It is noted that various formal definitions exist to characterize exchange capacity, the total solute concentration in the adsorbed phase. According to Helfferich (8), ion exchange capacity is the (constant) number of potentially ionized groups per amount of exchanger. The value of the apparent exchange capacity, the number of exchangeable counter ions per amount of exchanger, depends on the experimental conditions. Finally, the sorption capacity is the total amount of solute taken up by sorption rather than ion exchange, per amount of exchanger. The value of the sorption capacity depends

strongly on the experimental conditions. The overall sorptive capacity is the combined exchange and sorption capacity. In soil science, exchange capacity is referred to as anion and cation exchange capacity (AEC and CEC, respectively). To evaluate what type of exchange capacity is actually involved, one should consider the method of determination. Frequently, no distinction is made between exchange as a result of the charge of the exchanger and sorption. For the purpose of solute transport modeling, this is not necessary. From now on, it is therefore understood that experimental CEC values quantify both theoretical ion exchange, as defined before, and sorption.

Values for the CEC vary substantially, depending on the method of determination (20). Although, they are widely used to characterize soils, these values are not always applicable to transport studies. Typically, the determination is performed via a two-stage process. The colloidal complex of the soil is first saturated with a selected cation, the saturating or resident cation, which is subsequently displaced by adding an extractant containing another cation at high concentration (3). The amount of displaced cation in the extracted solution is measured to obtain the exchange capacity in $cmol_c kg^{-1}$ (meq/100 g). If the anions are displaced as well, the amount of displaced anions can be used as a measure of the excess, i.e., non-adsorbed, resident cations. The difference between the total amount of resident cations and anions is the preferred way to obtain the CEC which characterizes the electric charge of the soil complex. However, part of the cations accumulate in the adsorbed phase via sorption

instead of ion exchange or they might form complexes with anions, rendering this method unsuitable to obtain a CEC which characterizes the overall amount of sorbed solute. Several methods to determine CEC were used in this study.

The exchange isotherm is determined by the selectivity of the exchange complex for ions in resident and incoming solutions. In general, the exchanger prefers *(8)*: (1) the ion of higher valence, (2) the ion with the smaller (solvated) equivalent volume, (3) the ion with the greater polarizability, (4) the ion which interacts more strongly with the exchanger, and (5) the ion which participates least in complex formation with the co-ion.

The determination of exchange isotherms is usually time consuming, and no analytical solutions exist for transport of non-linear exchanging solutes. In transport studies, the exchange is therefore quite often assumed to be linear. As noted earlier, this assumption might be correct during partial exchange or for trace amounts of solute, but in general the assumption is not valid *(23)*. Therefore, the exchange isotherm needs to be determined, preferably with a method that is both relatively fast and for which the results are useful in transport studies. In this study, exchange isotherms were determined with a vacuum extraction method, VEM. In comparison with batch methods, BM, the VEM is simple, relatively quick, and inexpensive *(15)*. However, rather than saturating different samples with solutions of various ionic composition, the VEM was modified to determine the whole exchange isotherm with only one sample. This was accomplished by

subsequently changing the ionic composition of the eluent and determining the solute concentrations in the liquid and adsorbed phase for each change, thus yielding a number of points for the exchange isotherm.

MATERIALS AND METHODS

In order to study the determination of CEC and exchange isotherms for a wide range of soil types, a variety of soils and fraction sizes was used. Five Alabama soils were used in this study. Subsoils were collected at four Alabama Agricultural Experiment Station research units: the Wiregrass Substation at Headland (HEA); the Prattville Experiment Field (PRA); the Plant Breeding Unit at Tallassee (PBU); and the Upper Coastal Plain Substation at Winfield (WIN). The fifth soil was a Troup sand from Union Springs (US), which had a uniform pore size distribution (250-500 μm). Soil classifications are given in Table 1. These soils were also used to study transport in soil columns during subsequent experiments.

Table 1. Classification of Soils

Symbol	Location	Soil series	Family description
DOT	HEA	Dothan	Fine-loamy, siliceous, thermic Plinthic Paleudults
WIC	PBU	Wickham	Fine-loamy, mixed, thermic Typic Hapludults
SAV	WIN	Savannah	Fine-loamy, siliceous, thermic Typic Fragiudults
LUC	PRA	Lucedale	Fine-loamy, siliceous, thermic Rhodic Paleudults
TRO	US	Troup	Loamy, siliceous, thermic Grossarenic Paleudults

Cation Exchange Capacity

In this section the CEC determination using (1) a batch method (BM), (2) a vacuum extraction method (VEM), (3) breakthrough curves (BTC), and (4) Auburn University soil testing procedures (AU soil testing) will be discussed.

Batch Method

To eliminate the effect of organic matter on the CEC, part of each soil sample was pretreated with bleach to oxidize organic matter. From both the unbleached and bleached soil, two fractions were obtained via sieving: a fraction < 250 μm and a fraction ranging from 500 to 840 μm. The grain size of the Troup sand varied between 250 and 500 μm. Four 3.00-g subsamples of each unbleached fraction and two of each bleached fraction were placed in 50-cm^3 centrifuge tubes. Half of the bleached and unbleached samples were then saturated with $CaBr_2$ and the other half with KBr. Three washings with approximately 35 cm^3 of 0.01 M KBr and 0.005 M $CaBr_2$ were used to saturate the soil complex and obtain a homoionic system. Each time the solution was added, the suspension was shaken vigorously for 2 hours on a mechanical shaker and then centrifuged for 15 minutes at approximately 1500 rpm, upon which the supernatant liquid was decanted. The volume of the remaining soil solution ($V_{1,rem}$) was obtained gravimetrically (assuming a liquid density of 1 g cm^{-3}). The concentrations of Ca, K, and Na, yielding $(C_{Ca}+C_K+C_{Na})_{dec}$, of the final supernatant liquid were determined with the ICAP (Ca and K) and by atomic emission spectrometry (Na). Knowledge of the amount of the non-adsorbed cations eliminates the need to wash

them out during subsequent steps. Washings with water-ethanol mixtures, for instance, might influence the CEC value (5).

The next step in determining the CEC is to replace the adsorbed resident cations with an extractant. Approximately 30 cm^3 of a neutral 1 M NH_4OAc solution was added to each 3-g soil suspension, which was followed by shaking, centrifuging, and decanting. The concentrations of Ca, K, and also Na, yielding $(C_{Ca}+C_K+C_{Na})_{extr}$, were determined for each decanted solution with the ICAP or by atomic emission spectrometry (AES). Standard solutions, needed for these determinations, were made using 1 M NH_4OAc. To verify that complete exchange of K and Ca had occurred, the extraction procedure was repeated for some samples. No significant amounts of Ca, K, and Na were found, indicating that one extraction was sufficient. Again, the weight of the remaining soil solution ($V_{2,rem}$) was obtained after the extraction to determine the net volume of the extracting solution (V_{net}= decanted volume + $V_{2,rem}$ – $V_{1,rem}$).

The CEC of each 3-g sample could then be calculated from:

$$CEC = \frac{10}{3}\left[(C_{Ca}+C_K+C_{Na})_{extr}V_{net} - (C_{Ca}+C_K+C_{Na})_{dec}V_{1,rem}\right] \qquad (2)$$

where the units for C and V are mol_c m^{-3} and m^3, respectively.

Because the CEC is pH dependent, the pH of soil samples saturated with the different Br salts was determined. Solutions of 50 cm^3 0.01 M KBr, 0.01 M NaBr, or 0.005 M $CaBr_2$ were added to 30-g samples of unsieved, untreated soil. The suspensions were subsequently shaken for 2 hours and upon centrifugation the pH of the supernatant was determined with a combination electrode.

Vacuum Extraction Method

The CEC was also determined with a vacuum extraction system (Centurion International, Inc.) to displace the resident cation, in adsorbed and liquid phase, with NH_4OAc. The same soils and soil fractions were used as for the BM except that the bleaching was omitted. From each soil type, 5 g of air dry soil was put into a plastic syringe. The bottom of the syringe contained fiberglas and cotton to prevent loss of soil, while some fiberglas was placed on top of the sample to avoid splashing of the soil towards the sides of the syringe when the displacing solution was added. The (air) dry soil was first saturated with $CaBr_2$ by twice leaching 50 cm^3 of 0.005 M $CaBr_2$ through each sample. The $CaBr_2$ solution was supplied from a syringe situated on top of the one containing the soil while the effluent was collected in a syringe below the one containing the soil. By continuously withdrawing the plunger of the lower syringe, a slight vacuum was created which allowed extraction of the effluent. The speed of extraction was approximately 0.2 cm^3 min^{-1}. The amount of the remaining soil solution (V_{rem}) was determined gravimetrically, while the concentration of the resident cation in this solution was estimated from the concentration of the second effluent. Subsequently, two volumes of approximately 50 cm^3 1 M NH_4OAc (pH=7) were leached through each sample. The volumes of effluent plus the volumes of the remaining soil solution were again determined gravimetrically to yield two net extraction volumes $V_{1,extr}$ and $V_{2,extr}$. The sum of the Ca, K, and Na concentrations in all eluent, i.e., $(C_{Ca}+C_K+C_{Na})_{el}$, and effluent,

i.e., $(C_{Ca}+C_K+C_{Na})_{eff}$, solutions were obtained as indicated before. The procedure of saturation with $CaBr_2$ and extraction with NH_4OAc was repeated with NaBr and KBr solutions. The CEC for a system saturated with cation species i, was calculated from:

$$CEC_i = 2 \times \left\{ \left[(C_{Ca}+C_K+C_{Na})_{1,eff} - (C_{Ca}+C_K+C_{Na})_{1,el} \right] V_{1,extr} + \left[C_{Ca}+C_K+C_{Na})_{2,eff} - (C_{Ca}+C_K+C_{Na})_{2,el} \right] V_{2,extr} - C_i V_{rem} \right\}$$ (3)

where the units for C and V are the same as for Eq.(2) and $C_i V_{rem}$ denotes the amount of non-adsorbed species i prior to the displacement with NH_4OAc.

AU Soil Testing

Routine determinations of the CEC are well documented (3, 13) and will only be mentioned briefly. Two of these routine methods were also used to determine the CEC (9). First, the sum of cations displaced from the soil sample was determined as a measure of the CEC. Obviously, this is not a reliable method if a significant amount of soluble salts is present. The second method consisted of saturating the soil with 1 *M* NH_4OAc at pH=7. Excess salt was removed by washing with an ethanol-water mixture and was halted if no more NH_4 could be detected in the effluent solution. Next, the NH_4 was displaced by K, which was applied as a 10% KCl solution at pH=2.5. The amount of NH_4, representing the CEC, was measured by distillation and titration.

Breakthrough Curves

The determination of breakthrough curves (BTC's), commonly employed to determine dispersion coefficients and retardation factors (11), facilitates the determination of an effective value of the CEC. An obvious advantage is that the conditions under which the CEC is obtained and for which it is going to be used, viz. the description of reactive solute transport, are similar. These experiments involved Ca/K exchange at a total concentration ranging from 0.005 to 0.01 M. The bulk volume of soil in each column was approximately 600 cm^3. Since a much larger amount of soil was used in BTC experiments than for the previously discussed CEC determinations, BTC experiments are more likely to yield CEC values representative for natural soil systems. BTC experiments can also be used to approximate the adsorption isotherm (16).

These determinations considered binary systems in which the resident cation, with initial concentration C_o, was displaced by another cation also at concentration C_o. By observing the breakthrough curve for a step change in concentration at the inlet boundary, the holdup H for that soil column follows from:

$$H = \int_0^\infty (1 - C/C_o) \, dT \qquad (4)$$

where T is the number of pore volumes leached through the column and C/C_0 is the dimensionless exit concentration of the displacing solute. Van Genuchten and Wierenga (24) described how R can be determined from H. Alternatively, one can consider the initial amount of the resident

solute in the column, described with:

$$H = V(\theta C_O + \rho S) \tag{5}$$

where V is the volume of the column $[L^3]$ and all other symbols have been defined before. In case of linear exchange ($\partial S \approx CEC$ and $\partial C \approx C_O$), Eqs. (1) and (5) indicate that $R = H/(V\theta C_O)$. Once R is determined, an effective value for the CEC *(22)* can be computed using Eq. (1), where the slope of the exchange curve is approximated according to $\partial S/\partial C \approx CEC/C_O$. For a pulse type of displacement, an effective value for R can be found by comparing the movement of the solute relative to the movement of the solvent.

Exchange Isotherms

Exchange isotherms for the binary systems, with a constant total electrolyte level, were also obtained with the previously described VEM. Measurements were made on the same samples as used for the CEC determination.

The samples were first saturated with 0.005 *M* $CaBr_2$ and subsequently leached with solutions of equal total electrolyte level, but with decreasing $CaBr_2$ concentrations and increasing KBr concentrations. Each increment in eluent and effluent concentrations yielded a point on the exchange isotherm. For each increment, the "final" concentration of the adsorbed cation was calculated from the "initially" adsorbed concentration and application of the general mass balance principle for a particular cation A:

$$(V_{rem}\Delta C_A + m\Delta S_A)_{soil} = (VC_A)_{el} - (VC_A)_{eff} \tag{6}$$

where V_{rem} is the remaining volume of the liquid phase of the soil, m is the air dry weight of the soil, and C_A and S_A are the concentration of A in liquid and adsorbed phase, respectively. The left hand side of Eq.(6) denotes the change of the amount of A present in the soil and the right hand side is the net amount of A supplied to the soil.

The choice of the volume of the eluent, the extractant, is important. If the absolute amount of solute in the extractant is too small or too large compared to the amount present in the soil, the change in concentration in adsorbed and liquid phase cannot be adequately determined. To get an impression of how the effluent concentration behaves as a function of the volume of eluent, five volumes of approximately 10 cm^3 of a 0.0045 M Ca/0.001 M K solution were added to the feed reservoir and leached through the soil plug. After each extraction, the solution in the collection syringe was weighed and used to determine the Ca and K concentrations. The Ca and K concentrations are shown as a function of volume of effluent for four soil types in figures 1A and 1B, respectively. During the last extraction, eluent and effluent concentrations were roughly equal, although equality is not a necessary condition to obtain a point on the exchange isotherm. Based on this result, an eluent volume of 50 cm^3 was chosen for the first extraction of every increment in K concentration, followed by a second extraction with 20 cm^3 of eluent with the same concentration as the first eluent to determine the equilibrium concentration in the soil solution (see also the section Error Analysis). Referring to Eq.(6), it should be noted that all terms of

Ca in SOLUTION
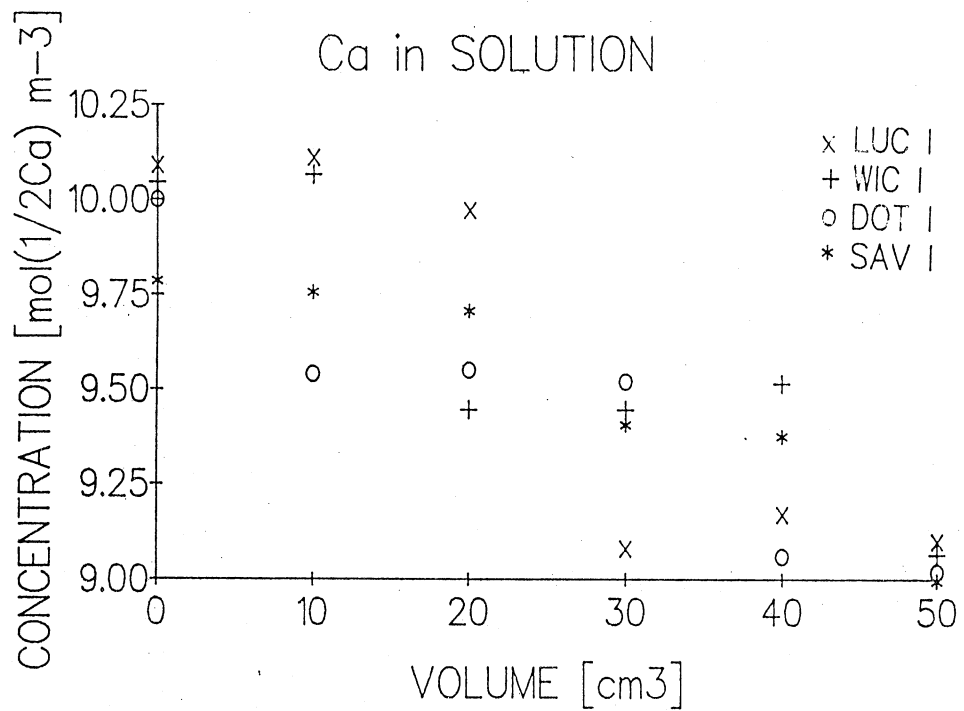
FIG. 1A. C_{Ca} of the effluent as a function of eluent volume.

K in SOLUTION
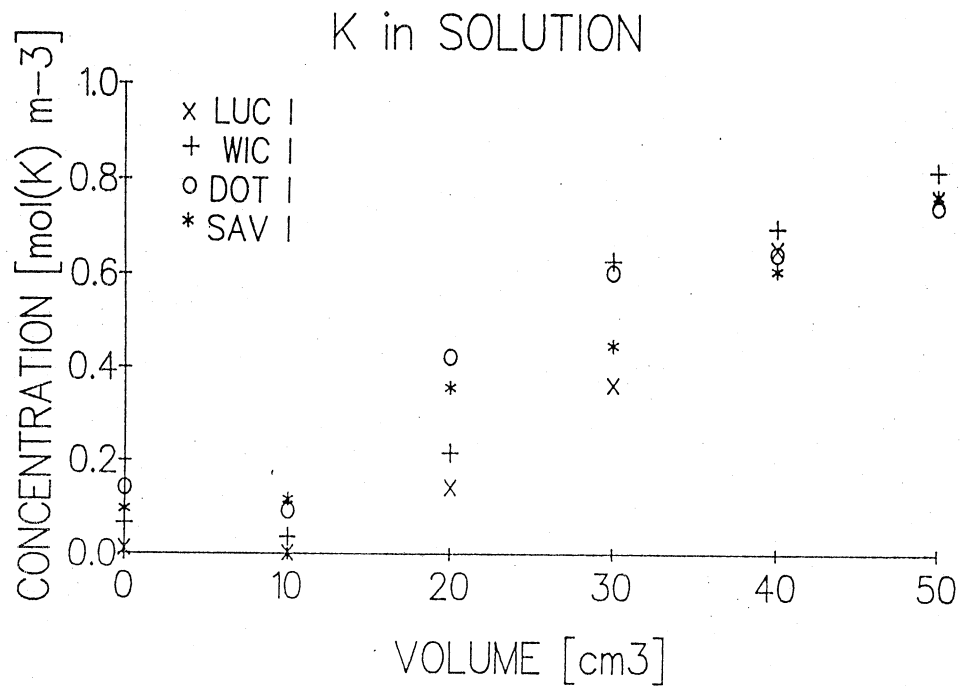
FIG. 1B. C_K of the effluent as a function of eluent volume.

the RHS can be measured directly. To obtain the terms of the LHS, it was assumed that the amount of solute in the soil, before the change in eluent concentration, was known (viz., $S_K = 0$ when K is introduced for the first time) and that C_A after the change in eluent concentration is approximately equal to the concentration of the second effluent (20 ml). S_A, after the change, remains then as the only unknown and can be solved for. This calculation procedure is repeated for each subsequent change in eluent concentration.

Because of the small volume of soil and the slow movement of the solution, channelling was assumed to be negligible. It should be noted that the volume of each input solution was assumed to be equal to the volume of each output solution. The volume of the solution absorbed by the soil varied between 5 and 8 cm^3, depending on soil type and cation and perhaps the duration of the extraction. This implies that 9 to 14 "pore volumes" were displaced during the total extraction for each step. The determination of the Ca/K exchange curve was completed, by using displacing solutions with a Ca/K ratio of 9/1, 7/3, 5/5, 3/7, 1/9, and 0/10 mol_c ($\frac{1}{2}$ Ca)/mol_c (K), respectively.

The volume of effluent, the volume of the soil solution, and the concentration of K and Ca in eluent and effluent were determined for each step. To determine the exchange isotherms for K and Na, solutions with a K/Na ratio of 9/1, 7/3, 5/5, 3/7, 1/9, and 0/10 mol_c (K)/mol_c (Na), respectively, were subsequently applied to the soil. Na and K concentrations were obtained with AES. Finally, solutions with a Na/Ca ratio of 9/1, 7/3, 5/5, 3/7, 1/9, and 0/10 mol_c (Na) mol_c /($\frac{1}{2}$Ca)

were leached through the soil to obtain the Na/Ca isotherms. The Na concentrations were determined with AES and the Ca concentrations with the ICAP.

For j additions of solutions with a particular cation ratio, the adsorbed concentration for a particular cation was obtained based on the general mass balance principle (Eq.(6)):

$$S_{fin} = S_{or} + 2 \times \left[(V_{rem,or}C_{rem,or} - V_{rem,fin}C_{rem,fin}) + \\ + \sum_{i=1}^{j} (V_{i,el}C_{i,el} - V_{i,eff}C_{i,eff}) \right] \tag{7}$$

S_{fin} and S_{or} are the final and original adsorbed concentrations expressed in the same units as CEC, $V_{rem,or}$ and $V_{rem,fin}$ are the volumes of soil solution before and after displacement, $C_{rem,or}$ and $C_{rem,fin}$ are the concentrations of the (remaining) soil solution before and after displacement, $V_{i,el}$ and $V_{i,eff}$ are the volumes of eluent and effluent solution during the ith-displacement, and $C_{i,el}$ and $C_{i,eff}$ are the concentrations of the eluent and effluent solution after the ith-displacement. The sum of the adsorbed concentrations corresponding to each increment can be used to determine the cation exchange capacity.

As noted before, two steps were used for each increment on the exchange isotherm with $V_{1,el} \approx V_{1,eff} \approx 50 cm^3$ and $V_{2,el} \approx V_{2,eff} \approx 20 cm^3$. Furthermore, $C_{rem,or}$ and $C_{rem,fin}$ are estimated with $C_{2,eff}$ before and after the increment in concentration of the eluent.

The adsorbed concentrations were calculated according to Eq.(7), based on measured values of concentrations and volumes of eluent. The

concentrations can be conveniently expressed in dimensionless form:

$$X_A = C_A/C_T$$
$$Y_A = S_A/S_T$$

$$(8)$$

where X_A is the dimensionless concentration of cation A in the liquid phase, C_A is the actual concentration in the liquid phase $[ML^{-3}]$, C_T is the sum of the concentrations of the competing cations $[ML^{-3}]$, Y_A is the dimensionless adsorbed concentration of cation A, S_A is the actual concentration of cation A in the adsorbed phase $[MM^{-1}]$, and S_T is the sum of the adsorbed concentrations of the competing cations $[MM^{-1}]$. It is convenient to use equivalent fractions, rather than mole fractions (Bolt, 1982). The units of C_A and S_A are $mol_c m^{-3}$ and $cmol_c kg^{-1}$, respectively.

According to Eq.(7), a value for the original adsorbed concentration is needed. Since the results of the CEC determinations already indicated a substantial variation in values of the adsorbed concentration at saturation, these concentrations are unsuitable as a starting value. On the other hand, if the system was saturated with the competing cation, the adsorbed concentration is obviously close to 0. Consider an experiment where cation B gradually displaces cation A. A starting point for the calculations of S_B was the taking of $S_B=0$, which is how the experiment was conducted. To calculate S_A, the starting point is $S_A=0$, which is at the end of the experiment. From a computational point of view, adsorption curves were determined for both A and B. Measurements for the last point of each curve indicated that the system was nearly saturated with B, i.e., $S_A=0$. The assumption that

the system was initially free of cation B, compared to A, seems reasonable as well. The sum of C_A and C_B was usually close to the prescribed value.

RESULTS AND DISCUSSION

Cation Exchange Capacity

The results of the pH measurements, along with values as determined routinely by the Auburn University Soil Testing Laboratory *(3)*, are listed in *Table* 2.

Table 2. pH of 50 cm^3 0.01 *M* Br Solutions
in Equilibrium with 30 g of Soil

Cation	DOT	WIC	SAV	LUC	TRO
	------------pH-------------				
Ca	5.8	6.2	4.7	6.3	5.5
Na	6.2	6.7	4.8	6.7	6.2
K	6.2	6.5	4.4	6.5	6.3
soil testing	5.1	6.1	4.8	6.6	6.3

The results for the CEC determination with the BM for a Ca and a K soil are given in table 3. Appendix A contains the volumes of soil solutions before and after the extractions, as well as the concentrations of K, Ca, and Na in the soil solutions before and after the extractions. The initial concentrations of Ca and K in the soil solutions were approximately 0.005 and 0.01 *M*, respectively. A second extraction showed no significant changes in CEC, and it was concluded that one extraction was sufficient. The differences between the 'bleached' and 'unbleached' soils were rather small in most cases,

Table 3. CEC Values Obtained by BM

Soil	Ca soil				K soil			
	b	b	u	Average	b	b	u	Average
	----------------------CEC [cmol$_c$/kg]----------------------							
DOTI	3.54	3.83	3.31	3.56	3.38	3.71	3.31	3.56
DOTII	1.25	1.41	1.47	1.38	1.15	1.22	1.40	1.26
WICI	4.25	4.28	4.21	4.25	4.06	3.98	4.13	4.06
WICII	4.61	4.64	4.46	4.45	4.19	4.27	4.27	4.24
SAVI	6.98	7.19	5.73	6.63	6.44	6.39	5.28	6.04
SAVII	5.03	4.91	4.63	4.86	5.25	5.36	-	5.31
LUCI	5.14	5.18	5.51	5.28	5.16	4.96	5.01	5.04
LUCII	2.76	2.91	3.07	2.91	2.72	2.72	2.79	2.74
TRO	0.14	0.09	0.14	0.12	0.10	0.09	0.11	0.10

b and u denote bleached and unbleached soil.
I   : fraction < 250 μm.
II : fraction 500-840 μm.

which was not surprising since they were subsoils. Therefore, the soils were not pretreated in further experiments.

The CEC values obtained by the VEM are presented in table 4. All data used for the CEC calculations are included in Appendix B.

Table 4. CEC Values Obtained by VEM

Cation	Soil Type								
	DOTI	DOTII	WICI	WICII	SAVI	SAVII	LUCI	LUCII	TRO
	----------------------CEC [cmol$_c$/kg]------------------								
Ca	5.76	3.58	6.22	5.92	8.64	6.68	7.08	5.24	1.40
K	5.41	2.51	4.91	5.12	7.33	6.57	7.05	3.76	-0.01
Na	3.34	1.76	3.56	2.88	6.03	4.54	5.19	2.25	-0.05

I   : fraction < 250 μm.
II : fraction 500-840 μm.

In order to analyze the effects of different methods and cations on the CEC value, the different treatments and treatment means are shown schematically in table 5.

Table 5. Schematic of Treatments

Method	Cation	Pre-treatment	No. of Samples	Treatment	
				No.	Mean
					$cmol_c/kg$
BM	Ca	b	18	1	3.79
		u	9	2	3.61
	K	b	18	3	3.62
		u	8	4	3.29
VEM	Ca	u	9	5	5.61
	K	u	9	6	4.74
	Na	u	9	7	3.28

Table 6 contains an analysis of variance for the data presented in table 3 and 4. Also included are a number of comparisons or contrasts of treatments.

Table 6. Analysis of Variance for CEC Data of tables 3 and 4

Source of Variation	df	F
Model	14	169.96[***]
Soil	8	261.07[***]
Treatment	6	48.47[***]
Contrasts		
1 BM vs. VEM (1,2,3,4 vs. 5,6,7)	1	105.07[***]
2 within BM Ca vs. K (1,2 vs. 3,4)	1	1.73[NS]
3 within BM b vs. u (1,3 vs. 2,4)	1	1.51[NS]
4 within VEM Ca vs. K (5 vs. 6)	1	25.14[***]
5 within VEM Ca & K vs. Na (5,6 vs. 7)	1	158.00[***]
Error	65	

[***] significant at the P=0.001 level.

The majority of the variation is associated with the differences between the soil types. The first contrast investigates differences between CEC values obtained with the VEM and BM. The values obtained with the VEM are significantly higher. Based on the data in Appendix A and B, it is assumed that the complex was initially saturated with the resident cation. Apparently, a more complete removal of the resident cation by the NH_4 was obtained with the VEM compared to the BM. For the VEM, the exchange was virtually completed during the first extraction with 50 ml NH_4OAc, which corresponds to the same liquid/solid ratio as for the BM. Although the pH of the extractant differed somewhat for the two procedures, the pH of the resident systems (soil and saturating cation) should be the same for a particular cation, implying that the amount of adsorbed cation should also be equal for a particular system as determined with the BM and the VEM. Hence. the observed differences in CEC for the two methods are not caused by differences in pH. However, for the VEM the liquid phase is continuously replaced and apparently allows for a more effective removal of the resident cations. If complete recovery of the adsorbed cations is desirable, the VEM is therefore to be preferred. On the other hand, channeling and the application of the eluent at a high velocity might prevent cations at all exchange sites to be in equilibrium with the extractant, which leads to a lower amount of extracted cations for the VEM.

The second and third contrasts compare the CEC values obtained with the BM for Ca- and K-saturated soils, and for bleached and unbleached soils, respectively. The difference in CEC between Ca and K

soil is negligible and the influence of bleaching on the CEC value is not significant.

The last two contrasts concern CEC values obtained with the VEM. CEC values for Ca soils are significantly larger than for K soils, which is somewhat in contradiction with the findings for the BM. Apparently, the differences occur only if the soil is completely saturated with the cation. According to the last contrast, CEC values for Na soils are substantially smaller than CEC values for K and Ca soils.

Several explanations may be given for the fact that the CEC, as obtained by the VEM, differs substantially for the three cations, table 4. These differences cannot be explained by the differences in pH resulting from saturating the systems with different cations. The pH value of the effluent solution during saturation with the resident cation, was about 5.5 for the Ca soils and 6.5 for the Na and K soils. Since the CEC generally decreases with diminishing pH, the higher CEC values for Ca soils is in contradiction with their lower pH values.

Rhue and Mansell (14) studied the effect of the pH on CEC and exchange isotherms using soil material from the surface horizon of a Cecil sandy loam. For a particular pH, the CEC for Ca soils was considerably higher than for Na soils. The data of these authors seem to suggest that at a pH of 8, the CEC became equal for both systems. These findings were explained on the basis of a higher exchange for Ca than for Na with H of the organic fraction of the soil. Exchange isotherms for Ca-Na and Ca-K exchange indicated that for the same

reason more Ca was adsorbed than K. However, the soils used in our study were low in organic matter. Table 2 indicated that organic matter hardly contributed to the CEC. Furthermore, the CEC for K soils was roughly equal to the CEC for Ca soils. Therefore it seems that differences in exchange properties were not caused by organic matter, but that perhaps a number of exchange sites were "accessible" for Ca and K but not for Na.

Next, the formation of complexes between the cations and bromide was considered. For some time, it has been known that the amount of adsorbed cations is influenced by the type of anions present, as was shown by Sposito et al. *(19)* for Cl. The following reactions might have occurred in the systems:

$$Ca^{2+} + Br^- \rightleftharpoons CaBr^+ \tag{9-a}$$

$$CaBr^+ + Br^- \rightleftharpoons CaBr_2^o \tag{9-b}$$

$$K^+ + Br^- \rightleftharpoons KBr^o \tag{9-c}$$

$$Na^+ + Br^- \rightleftharpoons NaBr^o \tag{9-d}$$
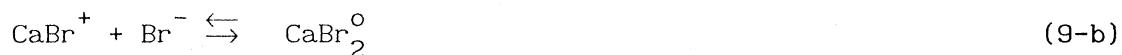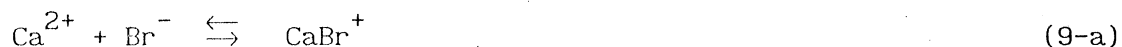
Unfortunately, very few thermodynamical data are available for these reactions, but more data are available for Cl. Complexation with K and Ca were considered as:

$$K^+ + Cl^- \rightleftharpoons KCl^o \qquad \log K^o = -0.7 \tag{10-a}$$

$$Ca^{2+} + Cl^- \rightleftharpoons CaCl^+ \qquad \log K^o = 0.42 \tag{10-b}$$
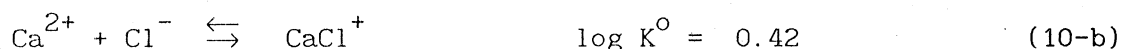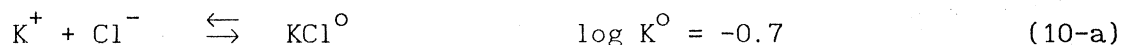
where the values for the thermodynamic equilibrium constant, K^o, are from Smith and Martell *(18)* and Sposito et al. *(19)*, respectively. Because the divalent Ca forms considerably more complexes than the monovalent K, it seems reasonable to ignore reactions (9-c) and (9-d).

To evaluate (9-a), consider Cu(II), for which Smith and Martell *(18)* provided the following:

$$Cu^{2+} + Cl^- \; \overset{\leftarrow}{\rightarrow} \; CuCl^+ \qquad\qquad \log K^o = 0.40 \qquad\qquad (11\text{-}a)$$

$$Cu^{2+} + Br^- \; \overset{\leftarrow}{\rightarrow} \; CuBr^+ \qquad\qquad \log K^o = -0.03 \qquad\qquad (11\text{-}b)$$
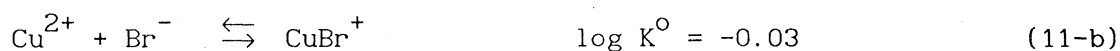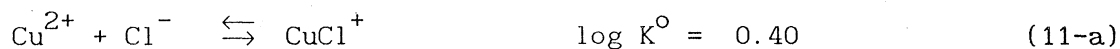
Equation (10-b) and (11-a) suggest that Ca and Cu form complexes to the same degree. Based on Eq.(11-b), this leads to the conclusion that $CaBr^+$ is less likely to be formed than $CaCl^+$, suggesting that the observed increase in CEC for Ca soils cannot be attributed to the formation of Ca complexes.

It should be noted that the soils used are all highly weathered, and have a fairly low base saturation *(6)*. Frequently, an effective cation exchange capacity, ECEC, is used to characterize the exchange capacity in these soils *(25)*. The value of the ECEC, determined as the sum of exchangeable bases, H and Al, is considerably lower than the value of the CEC determined after saturation with 1 *M* NH_4OAc *(17, 25)*. Obviously, this has its ramifications for the classification of these soils. Uehara and Gillman *(21)* pointed out that a large part of the surface charge is created by sorption of ions onto the surface. In other words, the charge of the surface is determined by the type of ion which is sorbed in excess. Differences in CEC values for soils saturated with Na, K, and Ca might therefore be attributed to differences in sorptive capacity.

Because the CEC values in these weathered soils depend so much on the experimental conditions, the use of "effective" CEC values is stressed. These values are to be obtained under similar conditions as

for which transport needs to be modeled. It is hoped that an improved soil characterization will benefit the simulation of solute transport in these soils.

Finally, table 7 contains the mean CEC values for the different soils obtained with the BM and VEM. With the exception of the Wickham series, the CEC is larger for the finer fraction.

Table 7. Mean CEC for Soils

Soil	No. of samples	Mean CEC	SD
		cmol$_c$/kg	
DOT I	9	3.95	0.946
DOT II	9	1.75	0.801
WIC I	9	4.40	0.768
WIC II	9	4.48	0.811
SAV I	9	6.67	1.002
SAV II	8	5.38	0.821
LUC I	9	5.59	0.852
LUC II	9	3.14	0.885
TRO	9	0.22	0.446

I : fraction < 250 μm.
II : fraction 500-840 μm.

Table 8 contains two sets of CEC values obtained with the AU soil testing procedures. The CEC values obtained from the sum of the displaced cations seem rather high, which were attributed to soluble or excess salts. The values obtained by means of NH_4OAc saturation correspond roughly to those determined with the BM, but are generally somewhat smaller than those obtained by the VEM if K was the saturating cation and generally considerably smaller if Ca was the saturating cation.

Table 8. CEC Values from AU Soil Testing

Method	Soil Type								
	DOTI	DOTII	WICI	WICII	SAVI	SAVII	LUCI	LUCII	TRO
	----------------------CEC [$cmol_c$/kg]-------------------								
Σ cations	8.13	4.54	6.27	7.92	9.64	7.12	10.37	3.82	1.35
NH_4OAc	4.08	3.50	6.27	3.92	6.34	6.22	4.58	5.18	0.90

I : fraction < 250 μm.
II : fraction 500-840 μm.

Values of the CEC derived from some selected breakthrough curves involving Ca and K are given in table 9. These CEC values, calculated under the assumption of linear exchange, are generally lower than those obtained with the methods previously described with the exception of the Troup soil. The results for TRO obtained with BTC's are probably more reliable than values from the other methods discussed previously because of the small amounts of soil used for the other determinations. A reasonable agreement exists with values obtained with the BM for other soils except for SAV I. Compared to the VEM, all values derived from breakthrough experiments are lower. Except for LUC II, the soil testing procedures yielded considerably higher CEC values. The lower CEC values derived from BTC experiments are presumably due to the fact that the extractant had a 100-fold smaller concentration. The use of CEC values, measured according to any of the procedures outlined for the batch method, vacuum extraction method and AU soil testing and applied to transport studies, is debatable because the R value is overestimated (Eq.(1)). R values obtained under the experimental

conditions for which solute transport needs to be modeled are to be preferred.

Table 9. CEC Values Determined with BTC Experiments

DOT I	DOT II	SAV I	LUC II	TRO	TRO
----------------cmol$_c$/kg----------------					
2.92	1.55	2.31	3.27	0.38	0.37

I : fraction < 250 μm
II : fraction 500-840 μm

Exchange Isotherms

The measurement of the exchange isotherms was carried out as described earlier. Appendix C contains measured concentrations of eluent and effluent as well as the volumes leached through and remaining in the soil plugs. Table 10 gives the sum of the adsorbed concentrations during the determination of the exchange curves of 9 soil types for all 7 cation ratios. These values carry a larger degree of uncertainty than the CEC determinations discussed before, because of the errors in the determination of the exchange curves. Considering the sand as a blank, the Ca/K system seemed to yield the most reliable results. Summation of the adsorbed concentrations resulted in smaller values for the CEC than for the determinations described under Cation Exchange Capacity, in the materials and methods section, with the exception of the Breakthrough Curve procedure. Apparently, the effective CEC values during displacement studies with low electrolyte levels of the extractant (e.g., 0.01 *M*) are smaller than those determined with the Batch Method, Vacuum Extraction Method, and AU Soil

Testing procedures (viz. 1 *M*). These low electrolyte levels also occur

in the "regular" solute displacement studies during the determination

of breakthrough curves, where the displacing solution served as an

extractant.

Table 10. Sum of Adsorbed Concentrations for Binary Systems
at Various Ratios of Solution Concentrations

Ratio	DOTI	DOTII	WICI	WICII	SAVI	SAVII	LUCI	LUCII	TRO
					$cmol_c/kg$				
C_{Na}/C_{Ca}									
0/10	2.10	0.43	3.76	3.01	5.47	4.33	5.39	2.29	-0.46
1/9	3.14	1.62	4.52	3.90	6.12	4.89	6.15	3.25	0.36
3/7	3.41	1.76	4.52	3.91	6.15	4.83	6.23	3.43	0.38
5/5	3.34	2.32	4.58	4.00	5.99	3.92	5.42	3.60	0.52
7/3	2.76	1.98	3.47	2.57	5.39	4.13	5.25	4.29	1.29
9/1	1.12	2.15	4.17	3.33	6.91	6.01	2.51	2.13	1.56
10/0	-0.90	1.48	2.79	3.34	6.81	5.06	1.74	1.07	1.50
C_{Ca}/C_K									
0/10	3.42	0.70	2.82	1.83	3.33	3.00	3.98	1.47	0.24
1/9	3.16	0.45	2.33	1.56	3.03	2.66	3.60	1.26	0.18
3/7	3.10	1.68	3.04	3.58	4.51	3.45	4.70	2.76	0.14
5/5	3.13	1.75	3.25	3.68	4.59	3.61	4.63	2.69	0.07
7/3	3.06	1.64	3.27	3.64	4.61	3.61	4.59	2.67	-0.02
9/1	2.98	1.63	3.30	3.62	4.55	3.60	4.59	2.60	-0.07
10/0	3.04	2.16	3.30	5.04	4.43	3.59	4.41	2.49	-0.05
C_K/C_{Na}									
0/10	3.04	2.16	2.54	2.55	3.93	2.69	3.31	1.04	0.34
1/9	3.26	1.99	2.82	2.69	3.95	2.64	3.66	1.39	0.49
3/7	3.44	2.27	2.89	2.91	4.27	2.70	4.28	2.31	0.61
5/5	4.60	2.64	3.64	2.81	4.88	3.19	4.82	2.99	1.18
7/3	4.04	3.93	2.76	3.31	3.54	3.81	4.57	1.44	0.73
9/1	3.01	2.42	2.79	3.79	3.98	3.85	4.52	3.36	2.15
10/0	3.42	2.78	3.43	5.98	4.37	4.91	5.09	3.43	2.35

I : fraction < 250 μm.
II : fraction 500-840 μm.

A SAS program, Appendix D, was used to correlate Y_A and X_A with a

cubic polynomial. The resulting curves, showing the dimensionless

amount of A in the adsorbed phase (Y_A) as a function of the dimensionless amount of A in the liquid phase (X_A), are given in figures 2 to 4 for Ca/K, K/Na, and Na/Ca, respectively. The adsorption complex clearly favors Ca and K over Na. For the Ca/K system, the cation for which $X_A < 0.5$ was favored, which was also found by Jensen (10) and derived theoretically by Harmsen (7). For the K/Na exchange, adsorption of K was favored in all instances.

Based on the results of the CEC determinations by the VEM, table 4, a pronounced increase in CEC can be expected if a Na soil becomes saturated with Ca. This influenced the determination of the exchange curves for Na/Ca exchange as can be seen in figure 4. At intermediate values for X_{Ca}, Y_{Ca} does not increase at the same rate as for very low values of X_{Ca}. For many Ca/Na isotherms, even a decrease in Y_{Ca} occurred with an increase in X_{Ca}. Similar findings were reported by Sposito et al. (19) for Na/Ca and Na/Mg exchange on Wyoming bentonite using Cl salts. These authors concluded that $CaCl^+$ and $MgCl^+$ were formed, which are adsorbed favorably on the internal surfaces of montmorillonite, whereas Ca^{2+} and Mg^{2+} are adsorbed on the outer surfaces. In case ClO_4 salts were used, with negligible complexation, no change in total adsorbed concentration, S_T, was found. It is noted that, in analogy to CEC determinations, exchange curves might be obtained by displacing the anion as well in order to account for complexation. Ignoring the change in CEC, the Ca/Na isotherms suggest that a somewhat similar curve is found as for the Ca/K isotherms, except that Ca is adsorbed much more favorably for the Ca/Na system.

FIG.2. Exchange isotherms for Ca/K systems.

Ca & K exchange for Savannah I

$Y=-0.03+2.19X-4.37X^2+3.32X^3$

$r^2_{adj} =0.99$

(X axis: K in SOLUTION, Y axis: K in ADSORBED PHASE)

Ca & K exchange for Lucedale I

$Y= 1.97X-3.64X^2+2.75X^3$

$r^2_{adj} =0.99$

(X axis: K in SOLUTION, Y axis: K in ADSORBED PHASE)

Ca & K exchange for Savannah II

$Y=-0.02+2.22X-4.38X^2+3.25X^3$

$r^2_{adj} =0.99$

(X axis: K in SOLUTION, Y axis: K in ADSORBED PHASE)

Ca & K exchange for Lucedale II

$Y=-0.01+2.48X-4.94X^2+3.47X^3$

$r^2_{adj} =0.97$

(X axis: K in SOLUTION, Y axis: K in ADSORBED PHASE)

Ca & K exchange for Troup sand

$Y=-0.01+0.73X+1.82X^2-1.53X^3$

$r^2_{adj} =0.85$

(X axis: K in SOLUTION, Y axis: K in ADSORBED PHASE)

FIG.2. Exchange isotherms for Ca/K systems.

Na & K exchange for Dothan I

$Y=0.31X-0.42X^2+1.25X^3$

$r^2_{adj}=0.98$

Na in ADSORBED PHASE / Na in SOLUTION

Na & K exchange for Wickham I

$Y=-0.04+1.08X-2.25X^2+2.32X^3$

$r^2_{adj}=0.96$

Na in ADSORBED PHASE / Na in SOLUTION

Na & K exchange for Dothan II

$Y=0.01+1.22X-1.41X^2+1.19X^3$

$r^2_{adj}=0.98$

Na in ADSORBED PHASE / Na in SOLUTION

NA & K exchange for Wickham II

$Y=-0.02+0.53X-0.26X^2+0.81X^3$

$r^2_{adj}=0.99$

Na in ADSORBED PHASE / Na in SOLUTION

FIG.3. Exchange isotherms for K/Na systems.

Na & K exchange for Savannah I

$Y = 0.54X - 0.48X^2 + 1.06X^3$

$r^2_{adj} = 0.99$

Na & K exchange for Lucedale I

$Y = -0.01 + 0.08X + 0.24X^2 + 0.83X^3$

$r^2_{adj} = 0.99$

Na & K exchange for Savannah II

$Y = -0.01 + 1.15X - 2.15X^2 + 2.09X^3$

$r^2_{adj} = 0.99$

Na & K exchange for Lucedale II

$Y = -0.01 + 0.37X - 1.57X^2 + 2.33X^3$

$r^2_{adj} = 0.99$

Na & K exchange for Troup sand

$Y = 0.01 - 0.24X + 3.19X^2 - 1.94X^3$

$r^2_{adj} = 0.99$

FIG.3. Exchange isotherms for K/Na systems.

Na & Ca exchange for Dothan I

Ca in ADSORBED PHASE

$Y=2.32X-2.24X^2+0.94X^3$

$r^2_{adj}=0.92$

Ca in SOLUTION

Na & Ca exchange for Wickham I

Ca in ADSORBED PHASE

$Y=0.28+4.01X-7.66X^2+4.43X^3$

$r^2_{adj}=0.55$

Ca in SOLUTION

Na & Ca exchange for Dothan II

Ca in ADSORBED PHASE

$Y=0.02+3.90X-7.05X^2+4.21X^3$

$r^2_{adj}=0.74$

Ca in SOLUTION

Na & Ca exchange for Wickham II

Ca in ADSORBED PHASE

$Y=0.31+4.06X-8.12X^2+4.82X^3$

$r^2_{adj}=0.34$

Ca in SOLUTION

FIG.4. Exchange isotherms for Na/Ca systems.

Na & Ca exchange for Savannah I

$Y=0.16+4.67X-8.79X^2+5.02X^3$

$r^2_{adj}=0.82$

Na & Ca exchange for Lucedale I

$Y=0.02+6.14X-11.48X^2+6.37X^3$

$r^2_{adj}=0.91$

Na & Ca exchange for Savannah II

$Y=0.15+5.29X-9.83X^2+5.44X^3$

$r^2_{adj}=0.88$

Na & Ca exchange for Lucedale II

$Y=0.01+3.31X-4.63X^2+2.35X^3$

$r^2_{adj}=0.96$

Na & Ca exchange for Troup sand

$Y=0.10+0.64X-0.52X^2+0.86X^3$

$r^2_{adj}=0.84$

(All plots: x-axis "Ca in SOLUTION", y-axis "Ca in ADSORBED PHASE")

FIG. 4. Exchange isotherms for Na/Ca systems.

A more general description of the exchange process can be given from a thermodynamic point of view. Consider the following exchange reaction for cations A and B *(2)*:

$$\frac{1}{z_A} A_s + \frac{1}{z_B} B \overset{\leftarrow}{\rightarrow} \frac{1}{z_A} A + \frac{1}{z_B} B_s \tag{12}$$
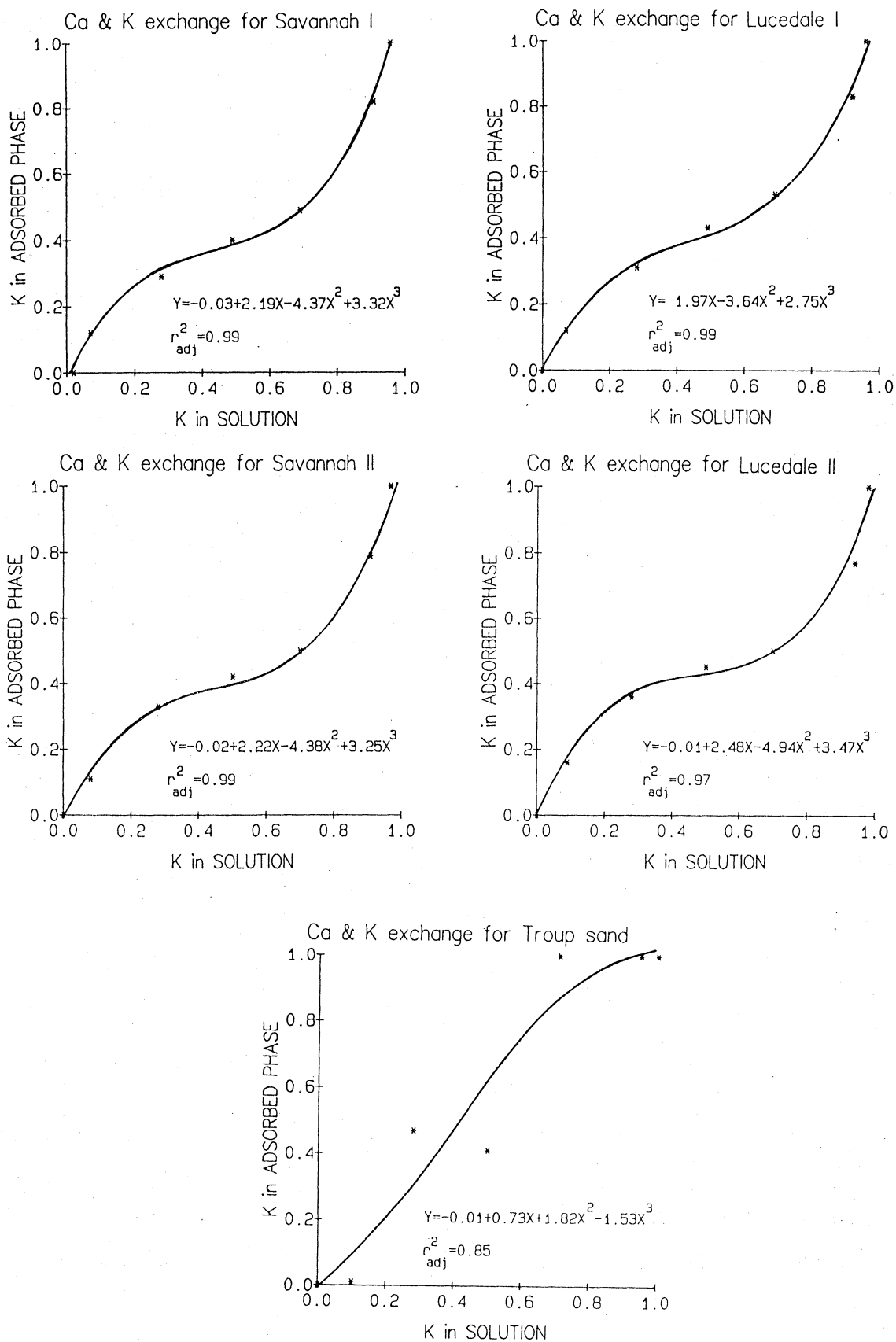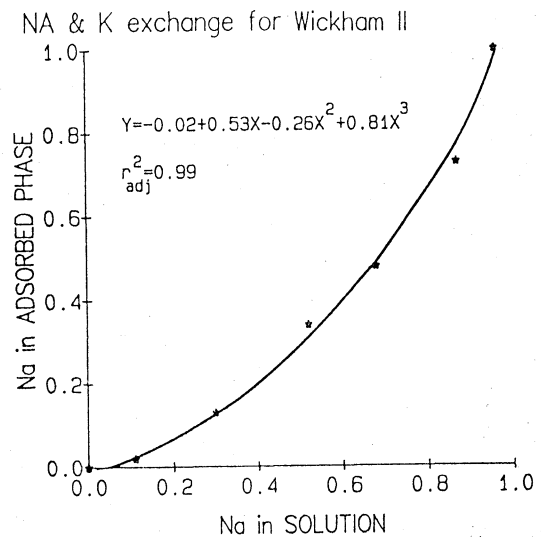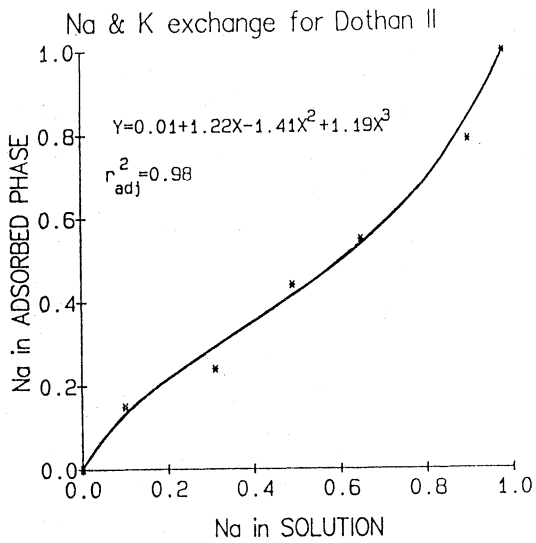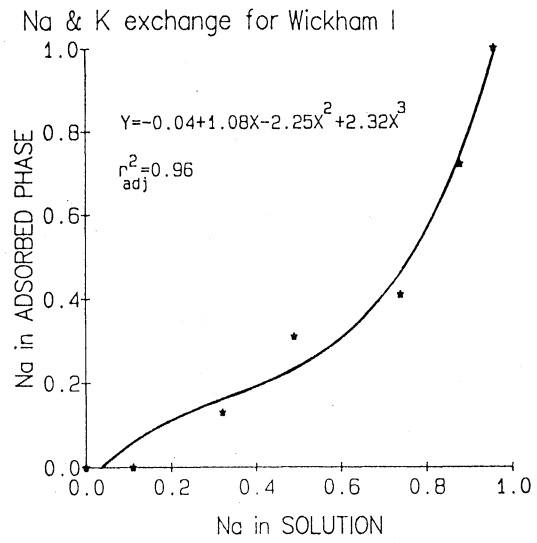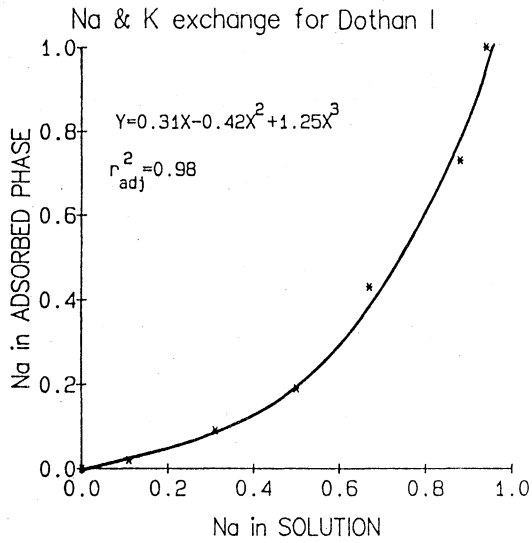
where the subscript s denotes the adsorbed phase and z is the valence of the cation. As mentioned before, no distinction is made between the free metal and metal-ligand complexes. The formation of these complexes is usually not considered for most exchange data reported to date. The reaction given by Eq. (12) is commonly characterized by the rational selectivity coefficient, K_N:

$$K_N = \frac{Y_B^{1/z_B} \; a_A^{1/z_A}}{Y_A^{1/z_A} \; a_B^{1/z_B}} \tag{13}$$

where a is the cation activity (the product of molar concentration and the activity coefficient). Mean values for the activity coefficients were calculated with the extended Debye-Hückel equation. Gaines and Thomas *(4)* derived the following relationship between the thermodynamic exchange constant for one equivalent of exchanger, K_{ex}^o, and K_N:

$$\ell n \; K_{ex}^o = -\left(\frac{1}{z_A} - \frac{1}{z_B} \right) + \int_0^1 \ell n \; K_N \; dY_B \tag{14}$$

It is noted that K_{ex}^o is constant over the whole concentration range. The value of K_{ex}^o depends only on temperature. The integral in Eq. (14) can be approximated as *(2)*: $\int_0^1 \ell n \; K_N \; dY_B \simeq \langle \ell n \; K_N \rangle$. The standard free enthalpy of the reaction is given by:

$$\Delta G^O_{ex} = - RT \, \ell n \, K^O_{ex} \qquad\qquad (15)$$

where ΔG^O_{ex} is the standard free enthalpy of the exchange reaction [J mol$^{-1}_c$]. Table 11 contains the values for $\ell n \, K^O_{ex}$ and ΔG^O_{ex}. Values for $<\ell n \, K_N>$ were determined as an average of $\ell n \, K_N$ over the range in solution concentration ratio of 1/9 to 9/1.

Table 11. Estimated Values for $\ell n \, K^O_{ex}$ and ΔG^O_{ex}

Soil	Ca/K†	K/Na	Na/Ca	Ca/K	K/Na	Na/Ca
	$\ell n \, K^O_{ex}$			ΔG^O_{ex} [kJ/mol$_c$]		
DOT I	2.05	-1.35	-0.67	-5.08	3.35	1.63
DOT II	2.04	-0.28	-1.49	-5.06	0.69	3.68
WIC I	2.69	-1.09	-1.62	-6.66	2.71	4.01
WIC II	2.40	-1.07	-1.05	-5.95	2.65	2.59
SAV I	2.11	-0.75	-1.06	-5.23	1.85	2.54
SAV II	2.08	-0.73	0.15	-5.14	1.81	-0.37
LUC I	2.16	-1.29	0.10	-5.36	3.20	-0.26
LUC II	2.11	-1.68	-1.13	-5.23	4.17	2.81

I : fraction < 250 μm.
II : fraction 500-840 μm.

† Resident ion A/displacing ion B.

The behavior of individual $\ell n \, K_N$ values is illustrated in figure 5A to 5C as a function of X_B. Figure 5A shows the behavior of $\ell n \, K_N$ when K displaces Ca. It is clear that $K_N > 1$ for all X_K. Therefore, the reaction given by Eq.(12) tends to the right and the complex favors K over Ca. When Na displaces K, figure 5B, the reaction tends to the left and the complex favors K over Na. The Na/Ca system, figure 5C, does not show a consistent dependency of $\ell n \, K_N$ on the adsorbed concentration. The values for K^O_{ex} in table 11 also indicate that K is adsorbed preferentially over Ca and Na, whereas the complex favors Na somewhat
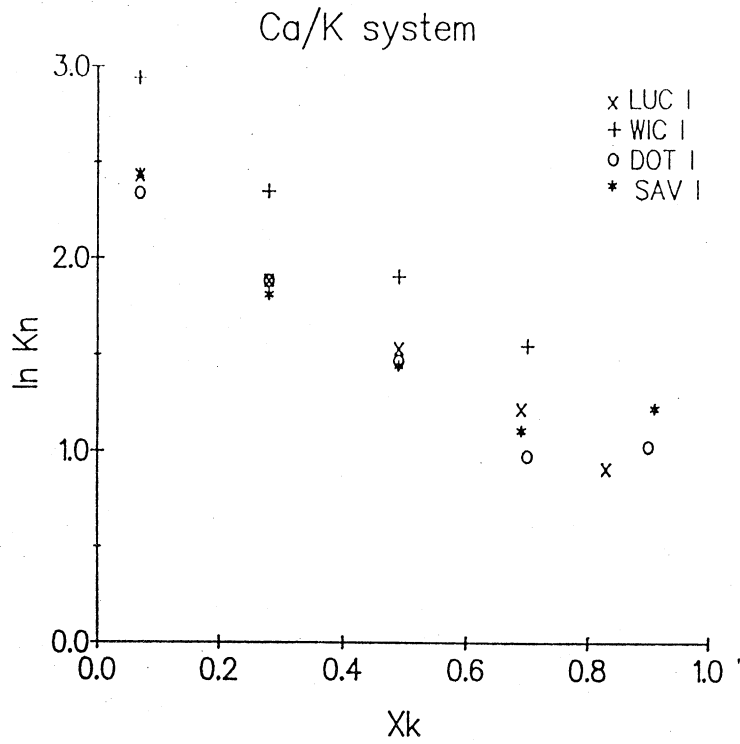
Ca/K system

FIG.5A. ℓn K_N as a function of X_K for Ca/K systems.
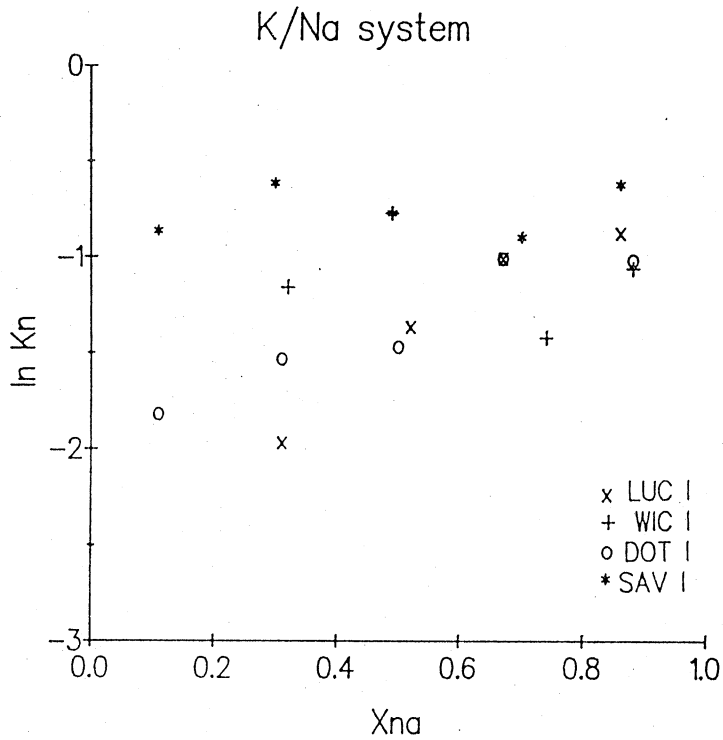
K/Na system

FIG.5B. ℓn K_N as a function of X_{Na} for K/Na systems.
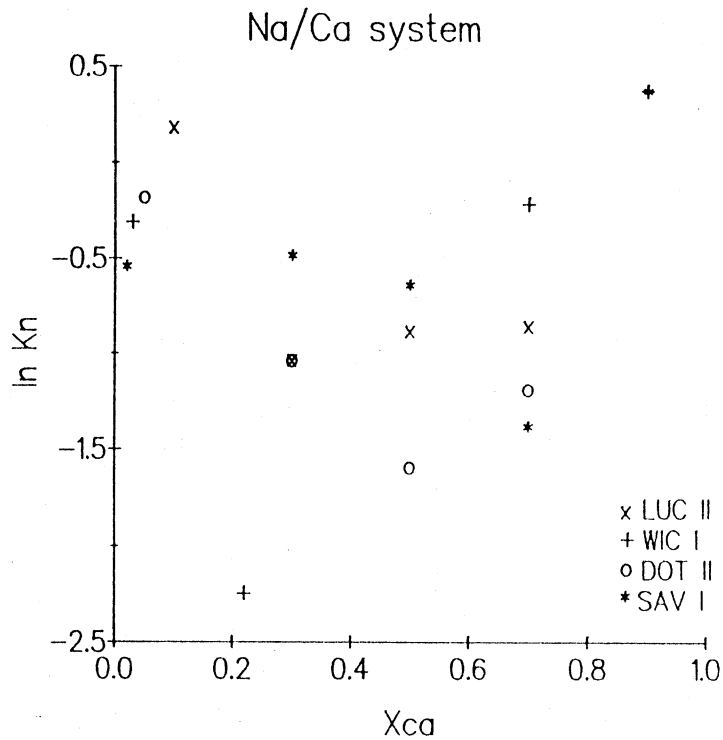
Na/Ca system

FIG.5C. $\ln K_N$ as a function of X_{Ca} for Na/Ca systems.

over Ca. It should be noted that these findings might not necessarily agree with the graphical results of figure 2, because different expressions for liquid and adsorbed concentration were used and because of the way the equilibrium constant was defined (viz., with Eq.(13) and (14)).

ERROR ANALYSIS

The determination of the exchange isotherm using increments in the solution concentration of the feed solution as described in the section on exchange isotherms, results in a larger error than for procedures which use one sample for each point on the isotherm. Two reasons can be pointed out in this respect:

- The absolute amounts of cations displaced/exchanged will be smaller for the "increment" method than for regular methods, where every point of the isotherm is obtained with a different sample, resulting in a larger relative error for the first method.

- The error of the adsorbed concentration in the increment method is cumulative, since the value of a previous adsorbed concentration is used to calculate the present value. Furthermore, the adsorbed concentration is determined in an indirect way, based on various solution concentrations and volumes of input, output, and resident solutions, all of which have some degree of error associated with them.

Obviously, these errors are a drawback of the increment method. However, an advantage of the stepwise adsorption of A/desorption of B is a reduction in time. Extraction of the "old" resident ions and saturation with the "new" resident ions takes place simultaneously. In addition, more efficient use is being made of equipment and chemicals, only one sample is needed to determine an isotherm, and the method is convenient for replicate studies.

The errors can be minimized by choosing appropriate extraction volumes and concentration increments. These choices are subjected to

several constraints. First, the volume of eluent should be sufficient to ensure exchange equilibrium has been reached at the new concentration. For simplicity, this can be assumed to be true if eluent and effluent concentrations are equal. Second, the concentration of the eluent and the time averaged concentration of the effluent should exhibit a significant change to detect changes in the adsorbed concentrations. Therefore, the volume of eluent cannot be too large. The soils which we investigated possessed fairly low CEC values, which increases the relative error in the adsorbed concentration. The low electrolyte levels of the systems might have partially compensated for this effect. To study the contribution of individual errors to the total error in the adsorbed concentration, S, an error analysis was carried out.

The adsorbed concentration for a soil with mass m [kg], using two extractions at each increment as described before, is determined according to:

$$S = S_{or} + \frac{0.01}{m} \left[(V_{rem,or}C_{rem,or} - V_{rem,fin}C_{rem,fin}) + V_{1,eff}(C_{1,el} - C_{1,eff}) + V_{2,eff}(C_{2,el} - C_{2,eff}) \right] \qquad (16)$$

where S_{or} is the solute concentration in the adsorbed phase before the increment change in eluent concentration [$cmol_c\ kg^{-1}$] and the units for C and V are $mol_c\ m^{-3}$ and m^3, respectively. Furthermore, it was assumed that effluent and eluent volumes were equal for each increment. Using the first degree Taylor expansion for S=ƒ(a,b,c,..), the error in S, dS, can be approximated by:

$$dS = \frac{\partial f}{\partial a} da + \frac{\partial f}{\partial b} db + \frac{\partial f}{\partial c} dc + \ldots \ldots \tag{17}$$

where da, db, and dc are errors in the factors a, b, and c, respectively. Application to Eq.(16) yields the following:

$$
\begin{aligned}
dS = dS_{or} &+ \frac{0.01}{m}\Big[V_{rem,or}dC_{rem,or} + C_{rem,or}dV_{rem,or} + \\
&- V_{rem,fin}dC_{rem,fin} - C_{rem,fin}dV_{rem,fin} + V_{1,eff}(dC_{1,el} + \\
&+ dC_{1,eff}) + (C_{1,el} - C_{1,eff})dV_{1,eff} + V_{2,eff}(dC_{2,el} + \\
&+ dC_{2,eff}) + (C_{2,el} - C_{2,eff})dV_{2,eff}\Big] + \\
&+ \frac{dm}{m^2}\Big[V_{rem,or}C_{rem,or} - V_{rem,fin}C_{rem,fin} + \\
&+ V_{1,eff}(C_{1,el} - C_{1,eff}) + V_{2,eff}(C_{2,el} - C_{2,eff})\Big]
\end{aligned}
\tag{18}
$$

Note that the maximum error in VC, viz. $\pm dVC$, follows from $(V+dV)(C+dC)$ = $VC+CdV+VdC+dVdC$, where we assume $dVdC=0$.

As an example, the Na/Ca exchange curve for SAV I was used. Any other pair of cations or soil could have been used as well. Somewhat arbitrarily, the following errors were assigned:

$$dV = \pm\, 0.03 \times 10^{-6}\ m^3$$
$$dC = \pm\, (0.05 \pm 0.02C)\ mol_c\ m^{-3}$$
$$dS_{or} = \pm\, 0.25\ cmol_c\ kg^{-1}$$
$$dm = \pm\, 0.03 \times 10^{-3}\ kg$$

Table 12 contains the data used for the error calculation in S_{Ca}, using Eq.(16) to calculate S_{Ca} and Eq.(18) to determine dS_{Ca} using the maximum error in V, C, S_{or}, and m. The error increases quite rapidly for $X_{Ca}>0.5$, with a relative minimum at about $X_{Ca}=0.3$, as can be seen in the bottom line of table 12 as well as in figure 6, which shows the relative error as a function of X_{Ca}.

Table 12. Calculation of the Relative Error, $\frac{dS}{S}$, in S_{Ca}, Obtained from Data of the Na/Ca Exchange Curve for SAV I

X_{Ca}	0	0.1	0.3	0.5	0.7	0.9	1.0
$V_{rem,fin}$		7.73	7.77	7.80	7.80	7.81	7.81
$V_{rem,or}$		7.75	7.73	7.77	7.80	7.80	7.81
$V_{1,eff}$		53.40	50.14	54.95	56.22	57.85	56.68
$V_{2,eff}$		23.96	25.75	25.78	29.55	27.93	28.53
$C_{1,el}$		1.00	2.90	5.00	7.23	9.40	10.59
$C_{2,el}$		0.99	2.89	5.08	7.20	9.00	10.55
$C_{1,eff}$		0.01	0.45	4.17	6.43	8.81	10.22
$C_{2,eff}$		0.00	1.93	4.47	6.96	9.14	10.36
S_{Ca}	0.00	1.54	4.19	5.05	5.66	6.11	5.47
dS_{Ca}	0.25	0.15	0.40	0.84	1.48	2.28	3.19
$(dS/S)_{Ca}$ [%]		9.72	9.51	16.64	26.15	37.40	58.28

Units: V in cm^3, C in $mol_c\,m^{-3}$ and S in $cmol_c\,kg^{-1}$.
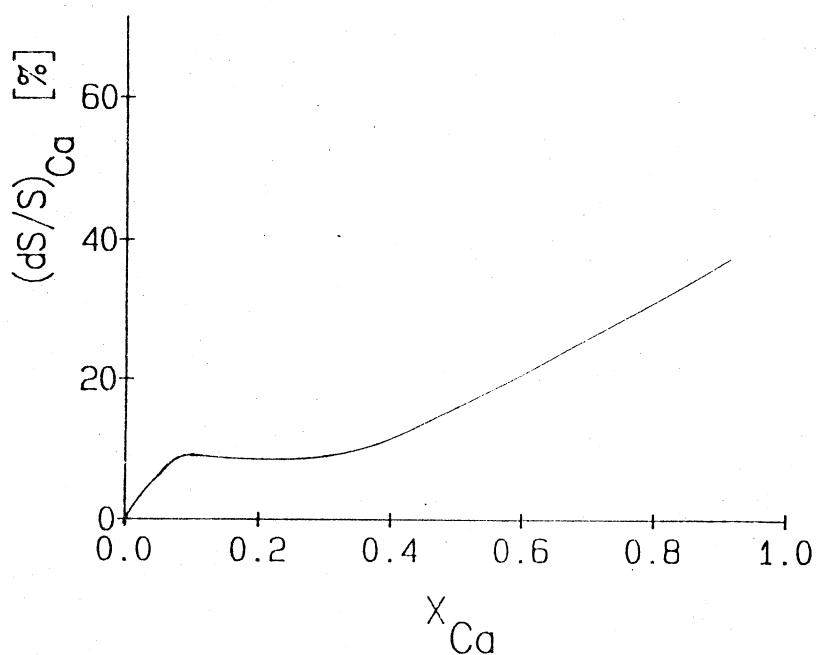
FIG.6. Theoretical error in the adsorbed concentration, $(dS/S)_{Ca}$, based on data for SAV I.

Also to consider is that the measured concentrations are flux-averaged values rather than volume-averaged values *(11)*. This is best illustrated by a hypothetical example, involving Ca/K exchange. For this idealized situation, we assume piston displacement and linear euilibrium exchange. Assume a dry dry soil weight of 5 g with a CEC of 5 $cmol_c kg^{-1}$ and the following hypothetical experimental values: $V_{rem,fin}=V_{rem,or}=6$ cm^3; $C_{Ca,or}=5$ $mol_c(\frac{1}{2} Ca)$ m^{-3}, $C_{K,or}= 5$ $mol_c(K)$ m^{-3}; $S_{Ca,or}= 2$ $cmol_c(\frac{1}{2} Ca)$ kg^{-1}, $S_{K,or}= 3$ $cmol_c(K)$ kg^{-1}. A feed solution with $C_{Ca}= 3$ $mol_c(\frac{1}{2} Ca)$ m^{-3} and $C_K = 7$ $mol_c(K)$ m^{-3} is applied. When the concentration of the soil solution reaches these values, the accompanying adsorbed concentrations are, presumably, $S_{Ca,fin}= 1$ $cmol_c(\frac{1}{2} Ca)$ kg^{-1} and $S_{K,fin}= 4$ $cmol_c(K)$ kg^{-1}.

The process is begun by considering only one extraction per increment in eluent concentration. Theoretically, a step change in effluent concentration occurs at the moment the invading solute establishes the prescribed change in concentrations in liquid and adsorbed phase of the soil, i.e., C_K changes from 5 to 7 $mol_c(K)$ m^{-3}. However, the effluent concentration is determined as a flux averaged concentration (i.e., $\int_0^{V_{eff}} C_K$ dV) and the step change will not be observed. Figure 7 shows the behavior of both concentration types. A similar comparison can be made between the adsorbed concentration calculated with Eq.(16) using one extraction, based on the theoretical resident concentration, and the one calculated with the hypothetical flux averaged concentration as observed in experiments. The differences in experimental and correct values for S_K are shown in figure 8.
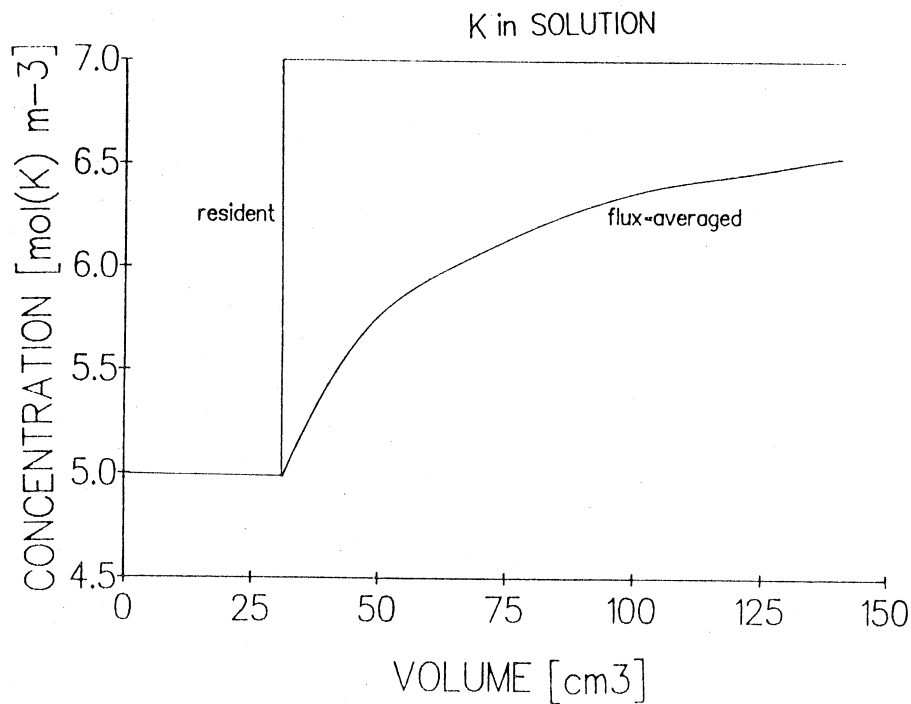
FIG.7. Flux-averaged and resident C_K as a function of effluent volume for a one step extraction.
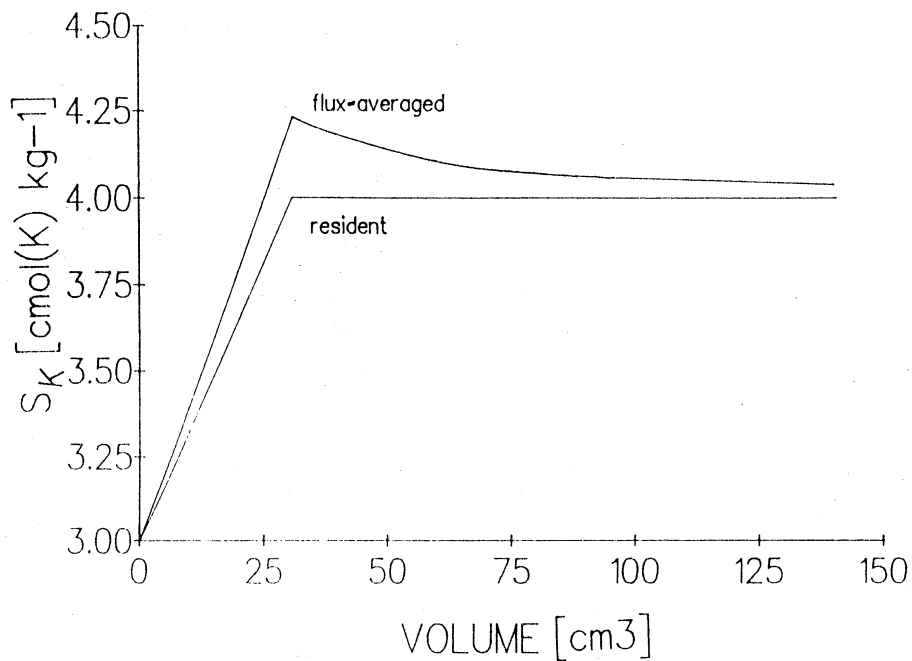
FIG.8. Adsorbed concentration, S_K, calculated with flux-averaged and resident C_K shown in figure 7.

The flux-averaged concentration of the effluent does not give a correct estimate of the concentration in the liquid phase of the soil. If this is not recognized, errors in S_K and C_K will be made, especially for smaller effluent volumes. For larger volumes, the flux-averaged concentration will approach the theoretical resident concentration, but this will lead to increased computational errors in S. To investigate this further the error in S_K, $(dS/S)_K$, was calculated according to Eq.(18) using flux-averaged concentrations. Table 13 contains the flux-averaged values for C_{eff} (figure 7) and the values for S_K based on this concentration (figure 8), as a function of the chosen extraction volume (V_{eff}), as well as the absolute and relative errors in S_K. The relative error with respect to the 'real' value of S_K, 4 $cmol_c(K)$ kg^{-1}, is also included.

Table 13. The Influence of the Extraction Volume, V_{eff}, on the Error in the Determination of S_K, $(dS/S)_K$, for a Hypothetical K/Ca System Using One Extraction

K/Ca	V_{eff}	C_{el}	C_{eff} res.	C_{eff} flux	dS_K	S_K	dS_K/S_K	$(S-S_{real})/S_{real}$
	cm^3	----	$mol_c\ m^{-3}$	---	$-cmol_c\ kg^{-1}-$		---------Pct.---------	
5/5	0	7.0	5.0	5.0	0.50	3.00	16.66	-25.00
7/3	10	7.0	5.0	5.0	0.60	3.40	17.72	-15.00
7/3	20	7.0	5.0	5.0	0.67	3.80	17.50	-5.00
7/3	25	7.0	5.0	5.0	0.70	4.00	17.41	0.00
7/3	31	7.0	5.0	5.0	0.73	4.24	17.30	6.00
7/3	40	7.0	7.0	5.5	0.80	4.19	18.99	4.75
7/3	60	7.0	7.0	6.0	0.93	4.12	22.69	3.00
7/3	80	7.0	7.0	6.2	1.07	4.09	26.21	2.25
7/3	100	7.0	7.0	6.4	1.21	4.07	29.71	1.75
7/3	120	7.0	7.0	6.5	1.35	4.06	33.14	1.50
7/3	140	7.0	7.0	6.6	1.48	4.05	36.60	1.25

FIG.9. Theoretical error in S_K, $(dS/S)_K$, using a flux-averaged value for C_K and deviations of S_K from the 'real' adsorbed concentration as a function of effluent volume for a one step extraction.

The results of table 13 are illustrated in figure 9, which contains both types of relative errors as a function of the volume of effluent. An increase in the extraction volume minimizes the difference between real and theoretically determined concentrations, but at the expense of an increased experimental error. For this hypothetical case the optimum displacement volume is approximately 31 cm^3, table 13.

The results can be improved by using a second extraction after the soil solution and adsorbed concentrations have reached their final values at the particular input concentration. In this way, the total extraction volume can be kept relatively small and the effluent concentration for the second extraction converges to the resident concentration, yielding a reliable estimate for the final concentration

in the soil. The constant volume of the second extraction was arbitrarily chosen as 20 cm^3.

Table 14 contains some of the relevant data to determine the errors associated with the two-step extraction using the volume of the first extraction as the independent variable. From table 14, one can determine what the error in S_K is for a chosen volume of the first extraction. Figure 10 shows the theoretical effluent concentrations after the first and second extraction ($C_{1,eff}$ and $C_{2,eff}$, respectively). It appears that for a small volume of the first extraction, $C_{2,eff}$ approaches the theoretical resident concentration after the soil is saturated with the new eluent. The adsorbed concentration, S_K, based on the two-step extraction is given in figure 11. Compared to the one-step extraction, figure 8, the 'real' S_K is approached considerably faster. Finally, the theoretical errors associated with this extraction, as a function of the volume of the first extraction, are given in figure 12. Based on these results, it was decided to use a volume of 50 cm^3 for the first extraction; dS/S is relatively small and the amount of solute is assumed to be sufficient to achieve complete displacement.

Table 14. The Influence of Extraction Volume $V_{1,eff}$ on the Error
in the Determination of S_K for a Hypothetical K/Ca
System Two Extractions

K/Ca	$V_{1,eff}$	$C_{1,eff}$ res	$C_{1,eff}$ ----flux-----	$C_{2,eff}$	dS_K	S_K	dS_K/S_K	$(S-S_{real})/S_{real}$
	cm^3	-----$mol_c\,m^{-3}$-------			-$cmol_c\,kg^{-1}$-		------Pct.------	
5/5	0	5.0	5.0	5.0	0.50	3.00	16.66	−25.00
7/3	5	5.0	5.0	5.0	0.57	4.00	14.36	0.00
7/3	10	5.0	5.0	5.0	0.61	4.20	14.42	5.00
7/3	11	5.0	5.0	5.0	0.61	4.24	14.43	6.00
7/3	15	5.0	5.0	5.4	0.64	4.19	15.19	4.80
7/3	20	5.0	5.0	5.9	0.67	4.13	16.17	3.30
7/3	25	5.0	5.0	6.4	0.70	4.07	17.18	1.80
7/3	30	5.0	5.0	6.9	0.73	4.01	18.23	0.30
7/3	31	5.0	5.0	7.0	0.74	4.00	18.44	0.00
7/3	35	7.0	5.2	7.0	0.77	4.00	19.14	−0.03
7/3	40	7.0	5.5	7.0	0.80	4.00	20.01	0.00
7/3	50	7.0	5.8	7.0	0.87	4.00	21.74	0.00
7/3	60	7.0	6.0	7.0	0.94	4.00	23.50	−0.10
7/3	80	7.0	6.2	7.0	1.08	3.99	26.96	−0.20
7/3	100	7.0	6.4	7.0	1.21	4.00	30.32	0.00
7/3	120	7.0	6.5	7.0	1.35	4.01	33.68	0.20

$C_{1,el} = C_{2,el} = 7\ mol_c(K)\ m^{-3}$, $V_{2,eff} = 20\ cm^3$.
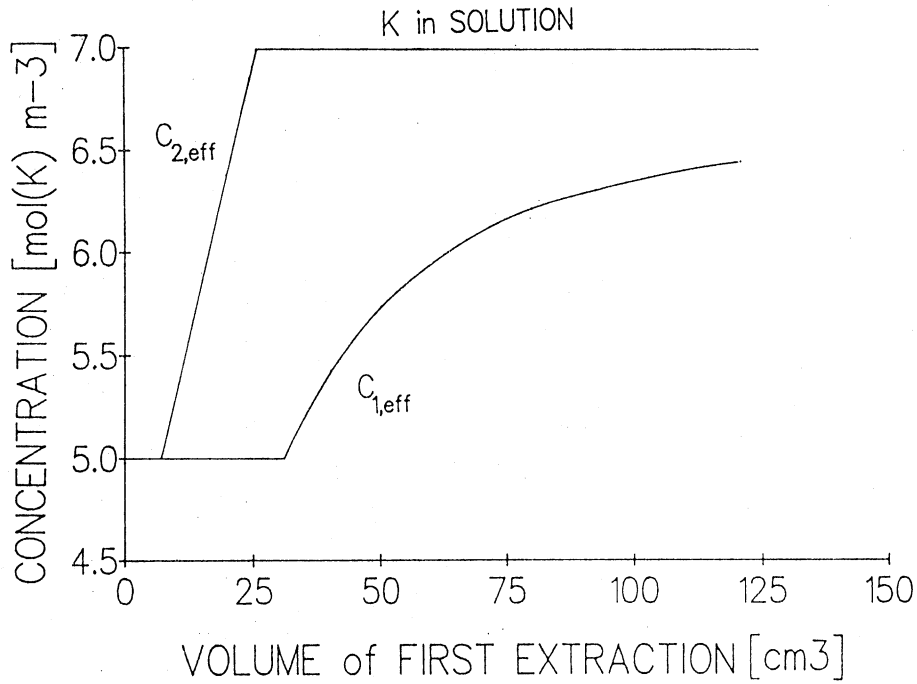
FIG. 10. Flux-averaged C_K of the effluent for the first $(C_{1,eff})$ and second extraction $(C_{2,eff})$ as a function of the volume of the first extraction $(V_{2,eff}=20 \text{ cm}^3)$.
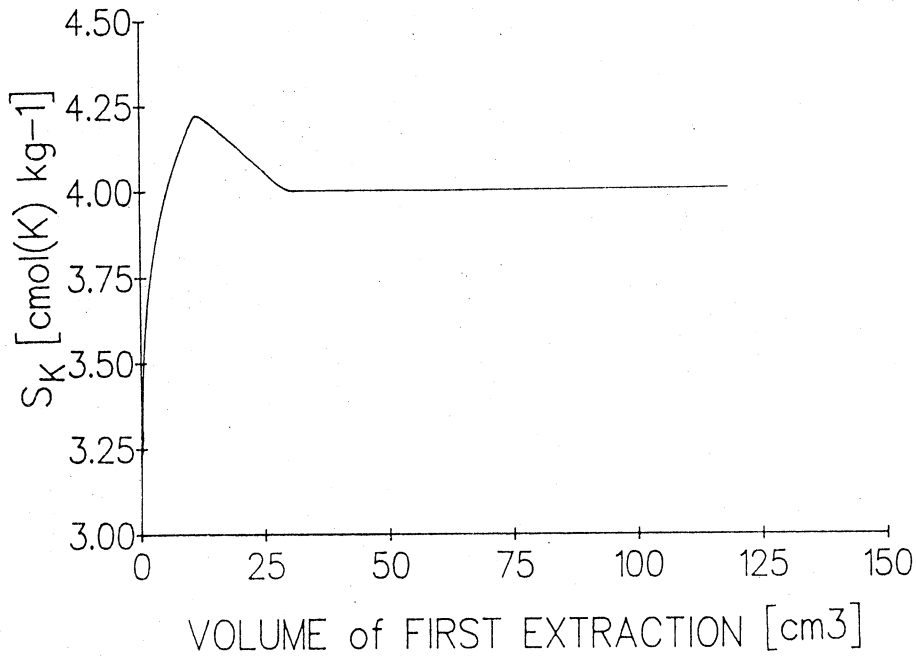
FIG. 11. Adsorbed concentration, S_K, calculated according to Eq. (16) using flux-averaged C_K shown in figure 10, as a function of the volume of the first extraction for a two-step extraction.
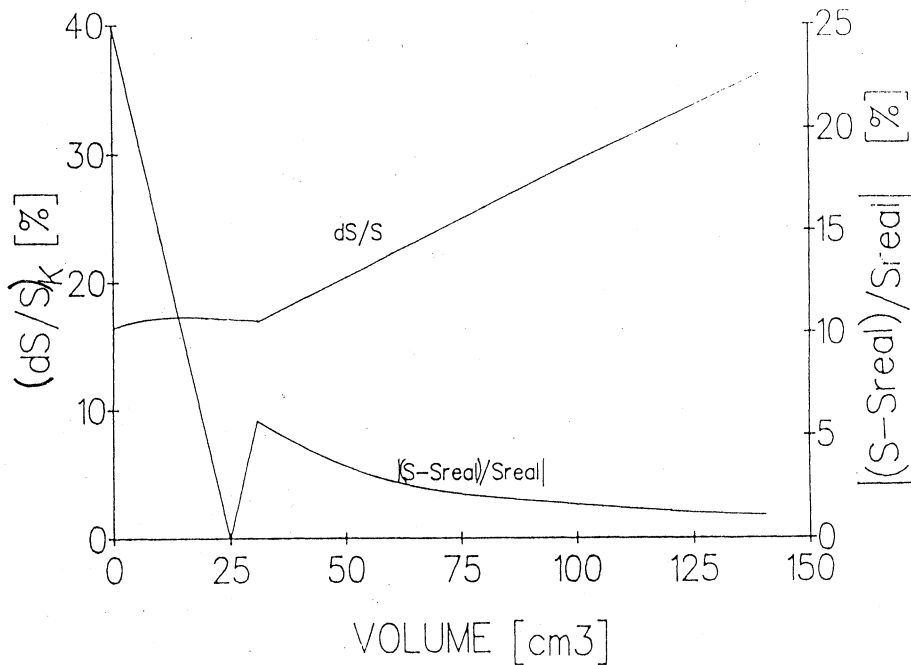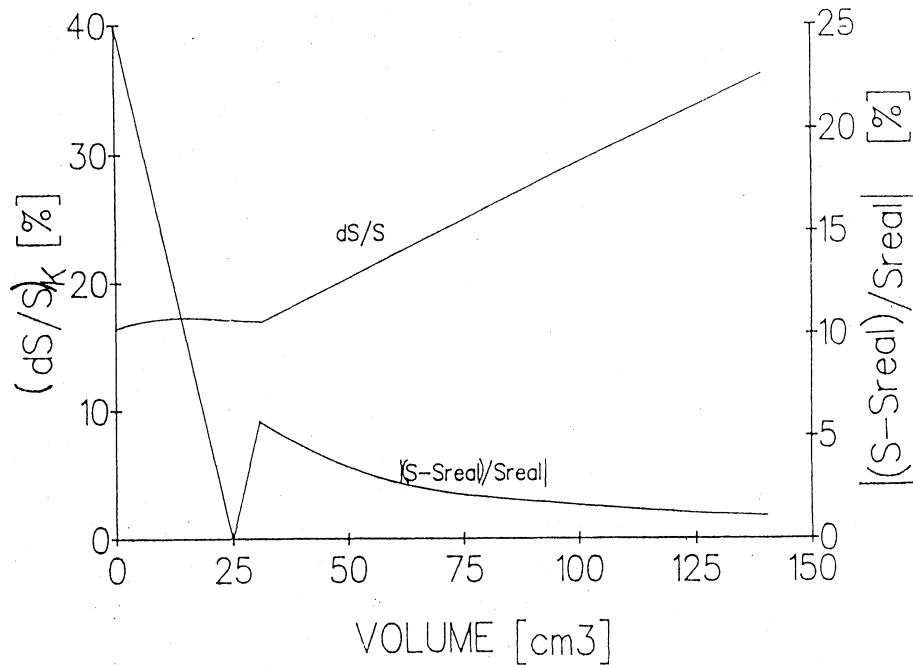
FIG. 12. Theoretical error in S_K, $(dS/S)_K$, using a flux-averaged value for C_K and deviations of S_K from the 'real' adsorbed concentration as a function of the volume of the first extraction for a two-step extraction.

SUMMARY AND CONCLUSIONS

A considerable amount of variation was found in the CEC values obtained by different methods, and different saturating cations. The VEM gave a more complete recovery of the cationic species than the BM. Values of the CEC determined under conditions similar to those during solute transport are generally lower than those obtained with common CEC determinations (e.g., BM, VEM, and AU soil testing) using extractants of high concentration (e.g., 1 M). This overestimation of the CEC could have serious ramifications when the movement of hazardous solutes needs to be predicted in time and space. Effective values of

the CEC should be used, determined under similar experimental conditions as the solute transport is studied. The effective CEC value characterizes the total amount of sorbed cation. No distinction between the various sorption mechanisms is required. The same is true for the determination of the exchange isotherms. The CEC for a Na soil is significantly less than for a K or a Ca soil, presumably because of different sorptive behavior.

Using increments in the solution concentration to determine exchange curves via the VEM appeared to be a feasible method. The errors inherent to this method could be reduced by using a two-step extraction method and appropriate extraction volumes. The Ca/K, Na/Ca, and K/Na isotherms showed pronounced differences for all soil types and seemed to be useful for further research involving the transport of reactive solutes in soil systems with similar chemical and physical characteristics. The independent determination of exchange properties, under similar conditions as the transport processes being studied, deserves careful attention because of their variability (CEC), i.e., depending on the method of determination, and non-linearity (exchange isotherm).

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Soil[†]	V_{rem}	C_{Ca}	C_K	C_{Na}	V_{net}	C_{Ca}	C_K	CEC
		Resident sol.				Decanted sol.[‡]		
DOT I-Ca-u	1.54	9.92	0.01	0.07	35.48	3.34	0.04	3.54
DOT I-Ca-u	1.78	9.80	0.03	0.07	35.33	3.65	0.05	3.83
DOT I-Ca-b	3.17	10.22	0.00	0.01	35.64	3.60	0.05	3.31
DOT I-K-u	1.63	0.26	9.67	0.06	35.53	0.33	2.93	3.38
DOT I-K-u	1.68	0.26	9.84	0.06	35.13	0.34	3.26	3.71
DOT I-K-b	2.07	0.26	9.95	0.07	35.39	0.35	3.01	3.31
DOT II-Ca-u	1.54	10.02	0.00	0.06	35.68	1.42	0.01	1.25
DOT II-Ca-u	1.55	10.24	0.00	0.06	35.18	1.59	0.02	1.41
DOT II-Ca-b	3.33	10.44	0.00	0.07	35.52	1.14	0.03	1.47
DOT II-K-u	1.49	0.06	10.18	0.06	35.67	0.04	1.31	1.15
DOT II-K-u	1.52	0.06	10.13	0.06	35.79	0.04	1.37	1.22
DOT II-K-b	1.45	0.08	10.08	0.06	39.21	0.06	1.34	1.40
WIC I-Ca-u	1.75	10.12	0.30	0.01	36.10	3.93	0.05	4.25
WIC I-Ca-u	1.72	9.92	0.00	0.01	35.63	3.99	0.05	4.29
WIC I-Ca-b	1.89	10.62	0.00	0.06	35.37	4.03	0.06	4.21
WIC I-K-u	1.98	0.32	9.78	0.12	35.33	0.60	3.37	4.06
WIC I-K-u	2.00	0.30	9.79	0.12	35.71	0.59	3.28	3.98
WIC I-K-b	1.94	0.30	9.87	0.01	37.04	0.55	3.28	4.13
WIC II-Ca-u	1.95	10.04	0.00	0.12	35.57	4.34	0.06	4.61
WIC II-Ca-u	1.85	9.54	0.00	0.12	35.89	4.26	0.06	4.64
WIC II-Ca-b	1.90	10.44	0.00	0.01	35.45	4.21	0.07	4.46
WIC II-K-u	2.14	0.30	9.80	0.12	35.70	0.62	3.46	4.19
WIC II-K-u	2.07	0.32	9.53	0.12	35.26	0.64	3.52	4.27
WIC II-K-b	2.03	0.32	9.90	0.12	35.37	0.62	3.55	4.27
SAV I-Ca-u	1.73	9.88	0.00	0.23	35.49	6.16	0.18	6.98
SAV I-Ca-u	1.91	10.00	0.00	0.23	36.03	6.27	0.21	7.19
SAV I-Ca-b	1.91	10.40	0.00	0.12	36.37	5.08	0.15	5.73
SAV I-K-u	1.75	0.30	9.65	0.22	35.42	0.79	5.11	6.44
SAV I-K-u	1.78	0.28	9.61	0.22	35.65	0.77	5.07	6.39
SAV I-K-b	1.91	0.60	9.77	0.23	36.29	0.80	4.07	5.28
SAV II-Ca-u	1.44	10.10	0.00	0.22	35.50	4.55	0.07	5.03
SAV II-Ca-u	1.52	10.36	0.00	0.22	35.62	4.48	0.06	4.91
SAV II-Ca-b	1.80	10.22	0.00	0.23	35.35	4.32	0.09	4.63
SAV II-K-u	1.57	0.24	9.80	0.22	35.70	0.56	4.25	5.25
SAV II-K-u	1.77	0.22	9.72	0.22	35.41	0.53	4.46	5.36
SAV II-K-b	1.51	0.32	9.53	0.22	35.65	1.11	0.38	1.33

(Continued)

APPENDIX A. Data for CEC Determination with the BM

Soil†	V_{rem}	C_{Ca}	C_K	C_{Na}	V_{net}	C_{Ca}	C_K	CEC
		resident sol.				decanted sol.‡		
LUC I-Ca-u	1.85	10.02	0.00	0.01	35.50	4.64	0.13	5.14
LUC I-Ca-u	1.58	10.68	0.01	0.01	35.98	4.62	0.11	5.18
LUC I-Ca-b	1.80	9.66	0.00	0.22	36.62	4.82	0.13	5.51
LUC I-K-u	1.73	0.36	9.56	0.01	35.53	0.86	3.93	5.16
LUC I-K-u	1.83	0.34	9.81	0.01	35.81	0.79	3.83	4.96
LUC I-K-b	1.99	0.38	9.72	0.01	35.34	0.46	3.86	5.01
LUC II-Ca-u	1.46	10.12	0.01	0.01	35.37	2.64	0.06	2.76
LUC II-Ca-u	1.41	10.00	0.00	0.01	36.19	2.70	0.05	2.91
LUC II-K-u	1.43	0.18	9.91	0.01	35.72	0.30	2.34	2.72
LUC II-Ca-b	1.28	10.44	0.00	0.01	35.72	2.84	0.07	3.07
LUC II-K-u	1.64	0.18	9.93	0.01	35.74	0.31	2.39	2.72
LUC II-K-b	1.34	0.16	9.72	0.01	35.61	0.35	2.33	2.79
TRO Ca-u	1.48	10.40	0.00	0.01	35.24	0.48	0.02	0.14
TRO Ca-u	1.50	10.26	0.00	0.01	35.63	0.45	0.01	0.09
TRO Ca-b	1.24	10.36	0.00	0.01	35.41	0.41	0.03	0.14
TRO K-u	1.18	0.02	10.14	0.01	35.46	0.02	0.36	0.10
TRO K-u	1.36	0.02	10.18	0.01	35.79	0.01	0.41	0.09
TRO K-b	1.15	0.02	10.01	0.01	35.28	0.00	0.37	0.11

† Soil type-saturating cation-bleached or unbleached.

‡ Na-concentration in extractant was estimated to be 0.05 $mol_c\ m^{-3}$ based on several measurements.

Units: V in cm^3, C in $mol_c\ m^{-3}$ and CEC in $cmol_c\ kg^{-1}$.

	DOT I	DOT II	WIC I	WIC II	SAV I	SAV II	LUC I	LUC II	TRO
Ca soil									
V_{rem}	6.46	6.91	7.02	7.25	7.78	7.11	6.82	7.25	5.52
$C_{Ca,rem}$ †	10	10	10	10	10	10	10	10	10
$C_{K,rem}$ †	0	0	0	0	0	0	0	0	0
$V_{1,eff}$	53.75	52.38	55.85	50.28	52.93	54.03	55.46	53.18	54.92
$C_{Ca,1,eff}$	6.38	4.76	6.62	6.64	9.01	7.34	7.43	6.17	2.26
$C_{K,1,eff}$	0.15	0.03	0.19	0.34	0.61	0.15	0.19	0.08	0.00
$V_{2,eff}$	53.33	53.87	52.10	52.13	51.46	52.30	53.78	53.15	51.37
$C_{Ca,2,eff}$	0.14	0.05	0.12	0.39	0.08	0.09	0.08	0.08	0.13
$C_{K,2,eff}$	0.00	0.00	0.00	0.04	0.03	0.02	0.01	0.01	0.00
CEC_{Ca}	5.76	3.58	6.22	5.92	8.64	6.68	7.08	5.24	1.40
K soil									
V_{rem}	6.47	7.03	7.02	7.35	7.81	7.18	6.86	7.32	5.36
$C_{Ca,rem}$	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
$C_{K,rem}$	9.79	9.61	9.96	9.49	9.58	9.59	9.83	9.83	9.75
$V_{1,eff}$	58.34	58.54	55.58	57.96	55.09	54.90	55.65	57.36	58.36
$C_{Ca,1,eff}$	0.05	0.01	0.02	0.00	0.03	0.05	0.07	0.07	0.00
$C_{K,1,eff}$	5.65	3.42	5.75	5.47	8.14	7.33	7.58	4.57	1.00
$V_{2,eff}$	50.50	48.51	50.62	50.55	47.98	49.88	47.99	49.34	51.07
$C_{Ca,2,eff}$	0.03	0.01	0.02	0.04	0.00	0.01	0.01	0.01	0.00
$C_{K,2,eff}$	0.13	0.00	0.00	0.32	0.00	0.00	0.00	0.00	0.00
CEC_{K}	5.41	2.51	4.91	5.12	7.33	6.57	7.05	3.76	-0.01
Na soil									
V_{rem}	6.46	6.91	7.02	7.25	7.78	7.11	6.82	7.25	5.52
$C_{Na,rem}$	10.62	10.55	10.55	9.95	10.09	9.67	9.59	9.83	10.64
$V_{Na,1,eff}$	48.37	50.02	47.48	50.59	49.05	49.49	48.70	50.97	48.87
$C_{Na,1,eff}$	4.87	3.18	5.24	3.80	7.75	5.90	6.64	3.57	1.15
$V_{Na,2,eff}$	52.36	54.95	53.04	54.56	53.64	52.30	52.38	55.33	55.41
$C_{Na,2,eff}$	0.00	0.03	0.06	0.44	0.00	0.07	0.03	0.03	0.00
CEC_{Na}	3.34	1.76	3.56	2.88	6.03	4.54	5.19	2.25	-0.05

† Estimate.
Units: C in $mol_c\ m^{-3}$, V in cm^3 and CEC in $cmol_c\ kg^{-1}$.

APPENDIX C. Data for Exchange Isotherms

	DOT I	DOT II	WIC I	WIC II	SAV I	SAV II	LUC I	LUC II	TRO
Ca/K=10/0									
V_{rem} †	6.78	6.98	7.10	7.71	7.66	7.49	6.64	8.42	5.57
$C_{Ca,rem}$ †	10.03	10.03	9.98	9.98	9.98	9.87	9.98	9.05	9.51
$C_{K,rem}$	0.15	0.15	0.08	0.13	0.16	0.01	0.05	0.01	0.00
Ca/K=9/1 $C_{Ca,el}$=9.04, $C_{K,el}$=0.99									
$V_{1,eff}$	10.24	9.73	10.39	9.88	10.17	9.96	9.68	10.42	9.95
$C_{Ca,1,eff}$	9.94	10.12	10.10	10.23	10.02	10.07	10.14	10.19	9.64
$C_{K,2,eff}$	0.09	0.11	0.03	0.02	0.11	0.19	0.05	0.11	0.46
$V_{2,eff}$	10.81	9.88	9.14	9.08	9.57	11.57	10.69	8.23	9.85
$C_{Ca,2,eff}$	9.56	9.66	10.02	10.28	9.75	9.95	9.99	9.87	9.29
$C_{K,2,eff}$	0.43	0.62	0.24	0.16	0.40	0.54	0.18	0.27	0.97
$V_{3,eff}$	8.97	9.78	9.20	9.92	9.37	11.34	9.80	9.74	9.25
$C_{Ca,3,eff}$	9.80	9.35	9.45	9.16	9.42	9.15	9.04	9.18	8.85
$C_{K,3,eff}$	0.60	0.87	0.63	0.53	0.49	0.48	0.42	0.62	0.98
$V_{4,eff}$	10.30	10.81	10.00	10.82	10.59	9.48	10.58	10.86	10.20
$C_{Ca,4,eff}$	9.09	9.01	9.53	9.26	9.42	9.17	9.32	9.18	8.87
$C_{K,4,eff}$	0.64	0.90	0.62	0.65	0.57	0.68	0.62	0.84	1.00
$V_{5,eff}$	9.24	9.73	10.16	9.76	10.07	11.34	9.94	9.61	9.59
$C_{Ca,5,eff}$	9.02	8.95	9.15	8.87	8.99	9.16	9.11	8.95	9.04
$C_{K,5,eff}$	0.68	0.96	0.71	0.73	0.70	0.83	0.74	0.90	1.02
V_{rem}	6.45	7.03	7.15	7.35	7.78	7.17	6.84	7.27	5.59
Ca/K=7/3 $C_{Ca,el}$=7.09, $C_{K,el}$=2.84									
$V_{1,eff}$	57.82	55.01	51.58	53.30	54.41	57.96	51.76	53.00	53.29
$C_{Ca,1,eff}$	7.72	6.65	7.86	6.46	6.90	7.21	7.29	6.58	7.32
$C_{K,1,eff}$	2.20	2.14	2.11	1.64	1.89	1.97	1.72	1.95	2.62
$V_{2,eff}$	33.60	33.27	34.96	34.75	33.64	34.36	33.00	33.90	36.19
$C_{Ca,2,eff}$	7.15	7.11	6.41	7.12	6.85	7.18	6.97	6.96	7.06
$C_{K,2,eff}$	2.78	2.80	2.54	2.62	2.67	2.77	2.68	2.75	2.81
V_{rem}	6.46	6.91	7.02	7.25	7.78	7.11	6.82	7.25	5.52

(Continued)

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APPENDIX C. Data for Exchange Isotherms

	DOT I	DOT II	WIC I	WIC II	SAV I	SAV II	LUC I	LUC II	TRO
Ca/K=5/5 $C_{Ca,el}$=5.09, $C_{K,el}$=5.01									
$V_{1,eff}$	58.36	57.16	57.45	58.08	58.31	58.06	58.31	58.01	57.93
$C_{Ca,1,eff}$	5.62	5.45	5.57	5.58	5.81	5.67	5.90	5.66	5.30
$C_{K,1,eff}$	4.52	4.68	4.48	4.51	4.33	4.42	4.33	4.60	4.93
$V_{2,eff}$	24.63	20.97	22.12	22.48	21.23	19.53	22.96	22.72	24.32
$C_{Ca,2,eff}$	5.24	5.10	5.14	5.28	5.15	5.10	5.23	5.12	5.10
$C_{K,2,eff}$	5.04	5.03	4.97	4.89	4.96	5.02	4.97	5.05	5.11
V_{rem}	6.60	6.90	7.02	7.40	7.77	7.12	6.52	7.28	5.36
Ca/K=3/7 $C_{Ca,el}$=3.07, $C_{K,el}$=7.36									
$V_{1,eff}$	54.95	55.53	51.20	50.00	49.78	54.00	53.91	49.95	52.15
$C_{Ca,1,eff}$	3.72	3.50	3.76	3.77	3.98	3.80	3.88	3.72	3.29
$C_{K,1,eff}$	6.70	6.98	6.62	6.67	6.37	6.60	6.51	6.71	7.18
$V_{2,eff}$	25.20	21.23	20.10	20.80	20.12	18.48	24.89	20.59	21.73
$C_{Ca,2,eff}$	3.09	3.03	3.09	3.18	3.21	3.12	3.20	3.08	3.04
$C_{K,2,eff}$	7.30	7.33	7.22	7.15	7.14	7.20	7.15	7.21	7.34
V_{rem}	6.61	6.91	6.98	7.31	7.71	7.06	6.58	7.23	5.30
Ca/K=1/9 $C_{Ca,el}$=0.51, $C_{K,el}$=9.40									
$V_{1,eff}$	49.13	50.81	50.04	49.56	55.11	48.39	52.75	49.04	49.50
$C_{Ca,1,eff}$	1.66	1.33	1.78	1.53	2.19	1.88	2.13	1.69	0.83
$C_{K,1,eff}$	8.34	8.65	8.17	8.47	7.82	8.10	7.81	8.36	9.16
$V_{2,eff}$	21.55	22.57	23.92	23.15	21.71	20.14	19.27	20.32	24.64
$C_{Ca,2,eff}$	0.94	0.53	0.69	0.89	0.85	0.88	0.81	0.60	0.52
$C_{K,2,eff}$	8.94	9.22	9.00	8.87	8.95	8.90	9.00	9.21	9.26
V_{rem}	6.58	6.95	7.16	7.34	7.72	7.08	6.63	7.10	5.34

APPENDIX C. Data for Exchange Isotherms

	DOT I	DOT II	WIC I	WIC II	SAV I	SAV II	LUC I	LUC II	TRO
Ca/K=0/10 $C_{Ca,el}=0.00$, $C_{K,el}=10.04$									
$V_{1,eff}$	50.37	54.70		53.66	54.18	50.38	50.16	52.60	52.29
$C_{Ca,1,eff}$	0.58	0.34	0.53	0.60	0.61	0.59	0.60	0.44	0.10
$C_{K,1,eff}$	9.64	9.94	9.74	9.58	9.60	9.53	9.66	9.77	10.04
$V_{2,eff}$	20.90	21.28		21.62	18.58	21.08	20.44	22.00	19.68
$C_{Ca,2,eff}$	0.30	0.10		0.36	0.41	0.33	0.41	0.22	0.02
$C_{K,2,eff}$	10.23	10.24	9.96	9.98	10.02	10.09	10.07	10.22	10.38
V_{rem}	6.61	6.95	7.10	7.39	7.77	7.07	6.65	7.19	5.32
Na/K=0/10‡									
Na/K=1/9 $C_{Na,el}=1.1$, $C_{K,el}=9.15$									
$V_{1,eff}$	54.75	53.90	53.91	54.75	52.95	54.28	56.19	52.41	55.71
$C_{Na,1,eff}$	0.85	0.90	0.85	0.85	0.80	0.85	0.85	0.80	0.95
$C_{K,1,eff}$	9.15	9.40	8.95	9.10	9.15	9.20	9.05	8.95	9.10
$V_{2,eff}$	25.45	28.10	24.68	28.86	25.76	27.02	23.68	26.83	27.06
$C_{Na,2,eff}$	1.15	1.05	1.10	1.15	1.15	1.15	1.05	1.10	1.15
$C_{K,2,eff}$	9.05	9.20	9.25	9.15	9.35	9.30	9.05	9.20	9.05
V_{rem}	6.51	6.93	7.07	7.38	7.72	7.08	6.71	7.37	5.34
Na/K=3/7 $C_{Na,el}=3.10$, $C_{K,el}=7.15$									
$V_{1,eff}$	51.07	48.84	54.29	53.77	54.48	51.59	51.52	51.76	52.12
$C_{Na,1,eff}$	2.65	2.50	2.60	2.60	2.55	2.65	2.10	2.50	2.85
$C_{K,1,eff}$	7.00	7.10	6.55	6.95	6.95	7.10	7.15	7.05	7.15
$V_{2,eff}$	29.34	29.59	26.87	29.28	25.72	29.16	23.97	25.35	25.13
$C_{Na,2,eff}$	3.10	3.15	3.10	3.05	3.00	3.15	3.25	3.10	3.20
$C_{K,2,eff}$	7.00	7.10	6.55	6.95	6.95	7.10	7.15	7.05	7.15
V_{rem}	6.51	6.94	7.07	7.37	7.71	7.07	6.77	7.35	5.31

(Continued)

APPENDIX C. Data for Exchange Isotherms

	DOT I	DOT II	WIC I	WIC II	SAV I	SAV II	LUC I	LUC II	TRO
Na/K=5/5 $C_{Na,el}$=5.20, $C_{K,el}$=5.15									
$V_{1,eff}$	54.02	53.73	53.19	55.13	51.37	53.70	50.09	52.27	51.45
$C_{Na,1,eff}$	4.40	4.80	4.60	4.80	4.35	4.50	4.40	4.75	4.90
$C_{K,1,eff}$	5.15	5.45	5.35	5.50	5.65	5.35	5.45	5.30	5.35
$V_{2,eff}$	20.11	23.58	25.34	26.97	23.96	24.13	23.94	22.86	23.74
$C_{Na,2,eff}$	4.80	4.75	4.70	5.40	4.75	5.35	5.30	4.65	4.55
$C_{K,2,eff}$	4.80	5.00	4.85	4.95	4.95	4.95	4.85	4.90	4.80
V_{rem}	6.50	6.91	7.07	7.35	7.75	6.91	6.77	7.35	5.42
Na/K=7/3 $C_{Na,el}$=7.10, $C_{K,el}$=3.35									
$V_{1,eff}$	55.83	57.62	56.84	55.42	54.50	54.29	53.29	55.68	54.37
$C_{Na,1,eff}$	6.45	7.05	6.85	6.55	6.95	6.15	6.35	6.85	6.95
$C_{K,1,eff}$	3.95	3.95	3.80	3.80	4.05	3.70	3.95	3.65	3.60
$V_{2,eff}$	32.87	32.26	32.07	33.95	33.07	30.01	29.34	31.04	30.77
$C_{Na,2,eff}$	6.95	4.60	7.65	6.25	7.30	6.80	6.80	8.45	7.05
$C_{K,2,eff}$	3.35	2.50	2.70	2.95	3.20	2.85	3.35	3.00	2.90
V_{rem}	6.51	6.89	7.08	7.37	7.67	7.02	6.87	7.36	5.43
Na/K=9/1 $C_{K,el}$=0.98									
$V_{1,eff}$	53.40	50.20	53.97	52.99	53.86	56.16	52.72	54.20	53.28
$C_{Na,1,eff}$	8.35	8.65	7.85	7.65	7.70	7.85	7.90	7.70	7.60
$C_{K,1,eff}$	2.40	2.05	2.25	2.05	2.55	2.20	2.35	2.00	1.45
$V_{2,eff}$	30.17	31.29	29.78	33.39	33.47	29.78	30.32	30.75	32.85
$C_{Na,2,eff}$	9.05	9.40	8.55	8.35	7.85	8.35	8.25	7.00	8.10
$C_{K,2,eff}$	1.20	1.02	1.20	1.20	1.25	1.30	1.35	1.10	1.25
V_{rem}	6.50	6.85	7.03	7.37	7.69	7.08	6.92	7.16	5.42

APPENDIX C. Data for Exchange Isotherms

	DOT I	DOT II	WIC I	WIC II	SAV I	SAV II	LUC I	LUC II	TRO
Na/K=10/0 $C_{na,el}=10.97$									
$V_{1,eff}$	52.29	54.34	56.50	55.18	51.42	54.46	56.24	56.44	57.64
$C_{Na,1,eff}$	9.10	9.35	8.85	7.40	8.90	8.40	8.85	9.10	9.55
$C_{K,1,eff}$	1.00	0.70	0.90	0.90	1.10	0.90	0.95	0.75	0.15
$V_{2,eff}$	23.47	27.03	25.99	28.99	24.74	27.63	28.09	26.27	27.36
$C_{Na,2,eff}$	9.40	10.02	9.76	9.81	9.47	9.93	9.60	10.19	10.91
$C_{K,2,eff}$	0.55	0.20	0.40	0.40	0.45	0.35	0.60	0.30	0.00
V_{rem}	6.47	6.91	7.07	7.49	7.75	7.09	6.95	7.24	5.42
Ca/Na=0/10§									
Ca/Na=1/9 $C_{Ca,el}=1.00$, $C_{Na,el}=9.03$									
$V_{1,eff}$	56.43	56.76	56.24	52.18	53.40	57.61	54.36	53.18	53.89
$C_{Ca,1,eff}$	0.05	0.16	0.11	0.08	0.01	0.00	0.00	0.00	0.83
$C_{Na,1,eff}$	8.90	9.45	9.30	9.60	9.70	9.35	9.55	9.35	9.10
$V_{2,eff}$	25.42	24.88	24.68	25.63	23.96	23.96	25.06	26.62	24.82
$C_{Ca,2,eff}$	0.09	0.58	0.03	0.18	0.00	0.09	0.00	0.07	0.99
$C_{Na,2,eff}$	8.80	9.30	9.10	10.60	10.55	9.80	9.80	9.60	9.30
V_{rem}	6.52	6.91	7.04	7.40	7.73	7.12	6.92	7.30	5.35
Ca/Na=3/7 $C_{Ca,el}=2.90$, $C_{Na,el}=6.41$									
$V_{1,eff}$	55.97	56.28	51.08	52.61	50.14	54.29	54.44	52.24	50.51
$C_{Ca,1,eff}$	1.69	2.47	1.48	1.99	0.45	1.43	0.52	1.58	2.77
$C_{Na,1,eff}$	6.50	7.00	8.85	8.00	9.75	8.95	7.60	5.90	6.80
$V_{2,eff}$	26.71	26.22	24.75	24.92	25.75	25.27	24.86	25.73	23.28
$C_{Ca,2,eff}$	2.61	2.99	2.23	2.60	1.93	2.05	1.58	2.75	2.77
$C_{Na,2,eff}$	6.05	6.40	6.50	7.10	8.60	8.15	5.55	6.25	6.70
V_{rem}	6.48	6.93	7.00	7.43	7.77	8.13	6.93	7.32	5.44

(Continued)

APPENDIX C. Data for Exchange Isotherms

	DOT I	DOT II	WIC I	WIC II	SAV I	SAV II	LUC I	LUC II	TRO
Ca/Na=5/5 $C_{Ca,el}$=5.08, $C_{Na,el}$=4.73									
$V_{1,eff}$	55.15	56.60	56.63	56.22	54.95	54.74	57.21	55.08	54.72
$C_{Ca,1,eff}$	4.66	4.69	4.51	4.40	4.17	4.15	3.92	4.52	4.91
$C_{Na,1,eff}$	4.35	4.80	4.80	4.55	5.45	5.80	4.85	5.10	4.50
$V_{2,eff}$	26.02	26.68	27.07	27.86	25.78	26.04	28.12	27.64	28.17
$C_{Ca,2,eff}$	5.09	4.86	4.18	4.06	4.47	4.98	5.30	5.03	4.68
$C_{Na,2,eff}$	4.46	4.42	4.14	4.63	4.47	4.86	4.97	5.46	6.44
V_{rem}	6.54	6.97	7.01	7.40	7.80	7.15	6.96	7.30	5.39
Ca/Na=7/3 $C_{Ca,el}$=7.23, $C_{Na,el}$=2.69									
$V_{1,eff}$	54.39	56.66	57.10	54.73	56.22	57.68	55.85	55.57	57.42
$C_{Ca,1,eff}$	6.87	6.86	6.42	6.57	6.43	6.37	6.40	6.74	6.93
$C_{Na,1,eff}$	3.20	3.60	3.30	3.50	3.00	2.80	2.85	3.25	3.35
$V_{2,eff}$	31.43	28.71	31.54	28.26	29.55	28.32	32.12	27.92	30.18
$C_{Ca,2,eff}$	7.21	7.14	7.15	6.86	6.96	7.01	7.19	7.19	7.02
$C_{Na,2,eff}$	2.95	3.15	3.45	3.25	3.85	3.40	3.35	3.55	3.25
V_{rem}	6.51	6.94	7.03	7.44	7.80	7.19	6.84	7.35	5.65
Ca/Na=9/1 $C_{Ca,el}$=9.26, $C_{Na,el}$=1.14									
$V_{1,eff}$	50.50	53.23	53.31	55.19	57.85	53.72	57.43	54.83	57.77
$C_{Ca,1,eff}$	8.88	9.03	8.89	8.96	8.81	8.97	8.98	8.97	9.19
$C_{Na,1,eff}$	1.55	1.65	1.70	1.65	1.85	1.65	1.70	1.75	1.45
$V_{2,eff}$	29.34	26.26	27.23	27.13	27.93	29.24	28.51	29.33	29.74
$C_{Ca,2,eff}$	9.17	9.22	9.34	9.16	9.14	9.25	9.32	9.25	9.29
$C_{Na,2,eff}$	1.80	1.25	1.10	1.20	1.30	1.05	1.10	1.30	1.15
V_{rem}	6.52	6.98	7.13	7.42	7.81	7.16	6.87	7.34	5.37

APPENDIX C. Data for Exchange Isotherms

	DOT I	DOT II	WIC I	WIC II	SAV I	SAV II	LUC I	LUC II	TRO
Ca/Na=10/0 $C_{Ca,el}$=10.55, $C_{Na,el}$=0.00									
$V_{1,eff}$	55.47	57.80	55.66	55.10	56.68	56.31	53.01	55.34	56.10
$C_{Ca,1,eff}$	10.55	10.56	10.18	10.27	10.22	10.16	10.25	10.41	10.34
$C_{Na,1,eff}$	0.18	0.12	0.20	0.22	0.19	0.17	0.22	0.16	0.06
$V_{2,eff}$	29.52	30.30	29.77	28.94	28.53	25.64	28.72	30.10	28.27
$C_{Ca,2,eff}$	10.50	10.63	10.58	10.55	10.36	10.37	10.49	10.59	10.55
$C_{Na,2,eff}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V_{rem}	6.51	6.99	6.97	7.43	7.81	7.15	6.76	7.30	5.51

† concentration is expressed in $mol_c\ m^{-3}$ and volume in cm^3.

‡ C_K and V_{rem} follow from the values at Ca/K=0/10, C_{Na}=0.

§ C_{Na} and V_{rem} follow from the values at Na/K=10/0, C_{Ca}=0.

APPENDIX D. SAS Program to Fit a Cubic Polynomial Through the Data to
Determine Exchange Isotherms

```
data feike;
input x y;
xsq=x*x;
xcu=x*x*x;
cards;
0 0
.1 .01
.3 .08
.5 .17
.7 .34
.9 .59
1.0 1.0
;
proc reg data=feike;
model y=x xsq xcu;
output out=yz p=pred l95=l95 u95=u95;
proc plot data=yz;
plot y*x='o' pred*x='p'
/overlay vpos=40 hpos=80;
run;
```