

# Cation Competition in a Natural Subsurface Material: Modeling of Sorption Equilibria

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Accurate models of cation exchange are a prerequisite for predicting the transport of cations in soils and groundwater aquifers. In this paper, we investigate the competitive sorption of two major cations, Ca<sup>2+</sup> and Na<sup>+</sup>, to a natural loamy soil material. The experimental data set is unique since competitive sorption isotherms of Ca<sup>2+</sup> and Na<sup>+</sup> were measured for both cations and over a wide range of conditions by two different techniques (i.e., classical batch and flow-through reactor). A few classical one-site cation-exchange equations did describe the data set poorly, while the Gaines–Thomas and the Vanselow models are able to model the data semiquantitatively despite the heterogeneity of the sorbent. A quantitative description of the data was possible with a distribution of cation-exchange selectivities. Multisite cation-exchange models allowing for noninteger exchange ratios between Na<sup>+</sup> and Ca<sup>2+</sup> provided an accurate description of the experimental data. Such multisite models are thermodynamically consistent and reflect the chemical heterogeneity of the natural soil material.

## Introduction

Partitioning of chemicals between the solid and liquid phase determines the fate of reactive chemicals in subsurface environments (1–5). Accurate predictions of the transport behavior of sorbing chemicals can be often achieved based on the knowledge of the sorption equilibria of the chemicals in question. The success of this task critically depends on the availability of a mathematical model that is able to capture the partitioning accurately. Cation exchange is a special case of competitive sorption and has been extensively studied.

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Such reactions are of fundamental importance in agricultural and environmental engineering problems, including irrigation, contaminant transport, management of saline soils, and artificial aquifer recharge. Accurate models describing competitive sorption of cations are needed, for example, for predicting the movement of interacting cation fronts through subsurface porous media (2). Such predictions are extremely sensitive to the accuracy of description of sorption equilibria, especially if several competing cations are present simultaneously (3).

In this paper, we investigate the competitive sorption to a natural, chemically heterogeneous soil material for the two major cations Ca<sup>2+</sup> and Na<sup>+</sup> by studying each cation individually over a wide range in solution composition. We are not aware of a comparable data set available in the literature. Classical one-site cation-exchange equations are compared with respect to their ability to describe the experimental data. While some of these models perform much better than others, we show that a satisfactory description of the data is not possible with any of these models. A quantitative description of the data can be obtained by introducing additional types of binding sites resulting in a distribution of cation-exchange selectivities. Such multisite models may prove useful for predicting multicomponent transport processes in chemically heterogeneous subsurface porous media. While empirical in nature, such an approach is likely to be more useful in practice than a mechanistic approach of representing environmental sorbents, such as soils or sediments, as mixtures of pure substances. To predict the sorption behavior of actual environmental sorbents, the mechanistic approach still faces insurmountable problems due to the molecular complexity of the environmental materials.

**Models for Binding of Major Cations: Cation-Exchange Conventions.** The binding of major cations (e.g., Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) to soils and sediments is commonly described by cation-exchange reactions (7, 8). The basic assumption behind this mechanism is that the binding sites are always occupied with one of the cations and that the existence of vacant binding sites can be neglected. The rationale behind this premise is that the negative surface charge of the exchanger phase is always balanced by a charge-equivalent amount of adsorbed cations (9, 10).

Let us consider the competitive binding of Na<sup>+</sup> and Ca<sup>2+</sup> in a binary cation system. Our aim is to model quantitatively the amount of bound cations  $q_{Na}$  and  $q_{Ca}$  (in moles per unit mass of sorbent) as a function of the corresponding activities in solution  $a_{Na}$  and  $a_{Ca}$  (in moles per unit volume of solvent). All models have the same functional form:

$$q_{Na} = S\phi_{Na}(a_{Na}, a_{Ca}) \quad (1)$$

$$q_{Ca} = S\phi_{Ca}(a_{Na}, a_{Ca}) \quad (2)$$

which is a product of the site concentration  $S$  (in moles per unit mass of sorbent) and dimensionless functions  $\phi_{Na}(a_{Na}, a_{Ca})$  and  $\phi_{Ca}(a_{Na}, a_{Ca})$ . These functions, which are referred to as the local isotherms, depend on the activities of both cations in solution. These activities must be evaluated on the basis of solution concentrations and activity coefficients, for example, using the Davies approach (11). In this paper, the formation of chloride complexes of Ca<sup>2+</sup> and Na<sup>+</sup> were also included in the calculations based on the stability constants reported by Smith and Martell (12).

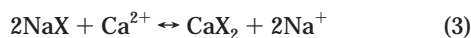
To derive a sorption isotherm, the appropriate mass action law must be formulated. The heterovalent exchange reaction

**TABLE 1. Binding Isotherms for 2:1 Exchange Reactions According to Different Conventions**

convention	binding isotherms <sup>a</sup>
Vanselow (1:2) ( $Q = S$ )	$q_{Ca} = \frac{S}{2} \left[ 1 - \left( \frac{a_{Na}^2}{a_{Na}^2 + 4Ka_{Ca}} \right)^{1/2} \right]$ $q_{Na} = S \left( \frac{a_{Na}^2}{a_{Na}^2 + 4Ka_{Ca}} \right)^{1/2}$
Gaines–Thomas (1:2) ( $Q = S$ )	$q_{Ca} = \frac{S}{2} \left\{ 1 + \frac{a_{Na}^2}{2Ka_{Ca}} - \left[ \left( 1 + \frac{a_{Na}^2}{2Ka_{Ca}} \right)^2 - 1 \right]^{1/2} \right\}$ $q_{Na} = S \left\{ \left[ \left( 1 + \frac{a_{Na}^2}{2Ka_{Ca}} \right)^2 - 1 \right]^{1/2} - \frac{a_{Na}^2}{2Ka_{Ca}} \right\}$
Cernik (1:2) ( $Q = 2S$ )	$q_{Ca} = S \left( \frac{Ka_{Ca}}{a_{Na}^2 + Ka_{Ca}} \right)$ $q_{Na} = 2S \left( \frac{a_{Na}^2}{a_{Na}^2 + Ka_{Ca}} \right)$
Gapon ( $Q = S$ )	$q_{Ca} = \frac{S}{2} \left( \frac{Ka_{Ca}^{1/2}}{a_{Na} + Ka_{Ca}^{1/2}} \right)$ $q_{Na} = S \left( \frac{a_{Na}}{a_{Na} + Ka_{Ca}^{1/2}} \right)$
Monovalent ( $Q = S$ )	$q_{Ca} = S \left( \frac{Ka_{Ca}}{a_{Na} + Ka_{Ca}} \right)$ $q_{Na} = S \left( \frac{a_{Na}}{a_{Na} + Ka_{Ca}} \right)$

<sup>a</sup> The isotherms for  $Ca^{2+}$  and  $Na^+$  express the bound amounts  $q_{Ca}$  and  $q_{Na}$  (moles per unit mass of sorbent) as a function of the corresponding activities  $a_{Ca}$  and  $a_{Na}$  (moles per liter). The total site concentration is denoted as  $S$ , and constant exchange capacity is denoted as  $Q = q_{Na} + 2q_{Ca}$ .

between  $Na^+$  and  $Ca^{2+}$  is commonly written as (9, 10)



where  $X$  is a surface site of charge  $-1$ . The total concentration of sites  $X$  is given by

$$S = q_{Na} + 2q_{Ca} \quad (4)$$

where  $S$  is the total site concentration in moles per unit mass of the solid. In this case, the quantity  $S$  is related to the cation-exchange capacity  $Q$  (in moles of charge equivalents per unit mass of sorbent) by  $Q = S$ .

In formulating the mass action laws for cation exchange, one usually assumes ideal exchange behavior and approximates the activity of adsorbed species either with mole fractions or equivalent fractions of bound cations (10, 13–15). The mole fractions are given by

$$x_{Na} = q_{Na} / (q_{Na} + q_{Ca}) \quad (5)$$

$$x_{Ca} = q_{Ca} / (q_{Na} + q_{Ca}) \quad (6)$$

with the condition  $x_{Na} + x_{Ca} = 1$ . Correspondingly, the equivalent (charge) fractions are written as

$$y_{Na} = q_{Na} / (q_{Na} + 2q_{Ca}) \quad (7)$$

$$y_{Ca} = 2q_{Ca} / (q_{Na} + 2q_{Ca}) \quad (8)$$

with  $y_{Na} + y_{Ca} = 1$ . The mass action law due to Vanselow (16) is based on reaction 3 and assumes that the activities of adsorbed species are given by their mole fractions, leading to

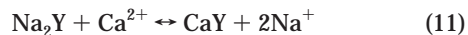
$$K = \frac{a_{Na}^2 x_{Ca}}{a_{Ca} x_{Na}^2} \quad (\text{Vanselow}) \quad (9)$$

where  $K$  is the exchange selectivity coefficient. Combination of the mass action law (eq 9) and the mass conservation law (eq 4) leads to the isotherms given in Table 1. The convention due to Gaines and Thomas (13) is also based on reaction 3 but employs equivalent fractions instead of mole fractions:

$$K = \frac{a_{Na}^2 y_{Ca}}{a_{Ca} y_{Na}^2} \quad (\text{Gaines–Thomas}) \quad (10)$$

The corresponding expression for the isotherm based on the Gaines–Thomas convention is again given in Table 1.

Alternatively, one can also consider the reaction



where  $Y$  now denotes a site of charge  $-2$  (8, 17). This reaction also represents a thermodynamically valid description of the exchange reaction. In this case, the total site concentration of sites  $Y$  is given by

$$S = q_{Na}/2 + q_{Ca} \quad (12)$$

and  $S$  is related to the conventional cation-exchange capacity  $Q$  by  $S = Q/2$ . Cernik et al. (17) have considered reaction 11 and formulated a mass action law in terms of the equivalent fractions:

$$K = \frac{a_{Na}^2 y_{Ca}}{a_{Ca} y_{Na}} \quad (\text{Cernik}) \quad (13)$$

The isotherm that results from the Cernik convention (eq 13) and the mass balance (eq 12) is given in Table 1. When

mole fractions are used in formulating the mass action law from reaction 3, the same isotherm is obtained but the corresponding selectivity coefficient  $K$  differs by a factor of 2.

Gapon (18) has proposed another approach that is not based on a rigorous reaction equation. The mass action law is written in terms of equivalent fractions in an ad-hoc fashion as

$$K = \frac{a_{\text{Na}} y_{\text{Ca}}}{a_{\text{Ca}}^{1/2} y_{\text{Na}}} \quad (\text{Gapon}) \quad (14)$$

Invoking the mass balance (eq 4), one can again derive the sorption isotherm for each cation (Table 1).

For the sake of completeness, let us also mention the 1:1 exchange isotherm. While one normally would not discuss this type of isotherm in the conjunction of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  exchange, consider the ternary exchange between  $\text{Ca}^{2+}$  and a pair of monovalent ions, such as  $\text{Na}^+$  and  $\text{H}^+$ , according to



where Z denotes a site of charge  $-2$ . Under the condition of constant  $\text{H}^+$  activity, the mass action law for this exchange reaction can be written as

$$K = \frac{a_{\text{Na}} y_{\text{Ca}}}{a_{\text{Ca}} y_{\text{Na}}} \quad (16)$$

Neglecting  $\text{H}^+$ , the total site concentration is then given by

$$S = q_{\text{Na}} + q_{\text{Ca}} \quad (17)$$

which would also be related to the conventional exchange capacity,  $Q$ , by  $S = Q/2$ . Combining eqs 16 and 17, the classical 1:1 exchange isotherm follows (see Table 1). These isotherms can be incorporated into chemical speciation codes with ease. The necessary stoichiometric matrixes are discussed in detail by Zachara and Westall (19).

**Multisite Approach.** Natural soils and sediments consist of a variety of different minerals and organic matter and are by nature chemically heterogeneous. Even a single mineral particle can have different types of cation-exchange sites exhibiting different exchange selectivities (20). Surface heterogeneity offers an intuitive explanation for the commonly observed “nonideal” behavior of cation exchange in soils, where exchange selectivities or exchange capacities may vary with solution conditions.

Several approaches have been developed to deal with chemical heterogeneity in sorption modeling (21–30). Such models were primarily applied for modeling proton and ion binding to humic substances. In the case of cation exchange, the Rothmund–Kornfeld model (28) or the power-exchange model (29) were proposed in order to account for such phenomena. In this paper, we discuss an alternative approach for describing the competitive binding of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  to a chemically heterogeneous soil material, namely, a discrete site affinity distribution model. Such models have the advantage of being easily compatible with general speciation codes generally applicable to describe ion binding to oxides, humic substances, and (as will be shown here) heterogeneous soil materials. The model concept is briefly outlined below; a more detailed discussion can be found in Cernik et al. (17).

Consider  $N$  different independent types of binding sites  $i$  ( $i = 1, 2, \dots, N$ ) described by pairs of local isotherms  $\phi_{\text{Ca},i}(a_{\text{Na}}, a_{\text{Ca}})$  and  $\phi_{\text{Na},i}(a_{\text{Na}}, a_{\text{Ca}})$  and a site concentration  $S_i$  (in mole per unit mass). Each of these isotherms is defined according to one of the cation-exchange conventions (Table 1), and the selectivity coefficients  $K_i$  enter as additional

parameters. The total amounts of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  sorbed can then be described by a summation of the local isotherms as

$$q_{\text{Ca}}(a_{\text{Ca}}, a_{\text{Na}}) = \sum_{i=1}^N S_i \phi_{\text{Ca},i}(a_{\text{Ca}}, a_{\text{Na}}) \quad (18)$$

$$q_{\text{Na}}(a_{\text{Ca}}, a_{\text{Na}}) = \sum_{i=1}^N S_i \phi_{\text{Na},i}(a_{\text{Ca}}, a_{\text{Na}}) \quad (19)$$

For a given combination of local isotherms, the corresponding set of site concentrations and the appropriate cation selectivity coefficients then define the affinity distribution model. The resulting isotherm will be thermodynamically consistent, since the local isotherms used in the model are thermodynamically consistent as well (17). Such a consistency relation states that a pair of isotherms are not independent in a multicomponent system.

The best-fit model parameters are determined by minimizing the weighted sum of squares  $\chi^2$ , which is a function of the differences between the experimental and the calculated adsorbed amounts. This function also depends on all total site concentrations  $S_1, S_2, \dots, S_N$  and the corresponding selectivity coefficients  $K_1, K_2, \dots, K_N$ . For a small number of sites, a classical least-squares schemes is usually sufficient to find the optimum set of parameters. However, as the number of sites entering the model becomes large, the classical optimization schemes become unstable and leads to convergence problems. Moreover, the resulting parameters values are unstable and may change substantially when small changes in the input data are made. These instabilities are well-known in the numerical mathematics literature and are related to the so-called ill-posed nature of this optimization problem. Various mathematical techniques are available to circumvent these difficulties. We have introduced constraints  $S_i \geq 0$  into the optimization scheme and used uniform spacing of the logarithms of the selectivity coefficients on a rather wide grid of 1.5. We further used regularization to bias the resulting affinity distribution toward a smooth function (regularization for smoothness). With these regularization techniques, the resulting parameters values are unique and stable. Additional details of the computational techniques are given elsewhere (17, 30).

## Materials and Methods

**Soil Material.** The soil material used for cation-exchange experiments was collected from the B horizon (15–25-cm depth) of a noncalcareous, acidic soil in northern Switzerland (Riedhof soil, dystric Eutrochrept). The moist soil material was gently broken into small aggregates, dried at 40 °C, and passed through a 2-mm sieve. For cation-exchange experiments, an aggregate size fraction between 63 and 400  $\mu\text{m}$  was separated by dry sieving. The soil material used in the experiments had silt loam texture, 6 g/kg organic carbon, pH 4.1 (in deionized water). The cation-exchange capacity determined by standard  $\text{NH}_4^+$  for  $\text{Ca}^{2+}$  exchange procedure is  $6.0 \times 10^{-5}$  mol/g, while we obtain  $5.9 \times 10^{-5}$  mol/g from fitting the sorption isotherms (see below). X-ray diffraction analysis showed that the clay fraction contained vermiculite, illite, kaolinite, and smaller amounts of quartz, chlorite, and goethite.

**Sorption Experiments.** Competitive sorption of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  to the soil material was investigated by measuring sorption isotherms of  $\text{Ca}^{2+}$  for several constant total NaCl electrolyte concentrations and sorption of  $\text{Na}^+$  for several constant total  $\text{CaCl}_2$  electrolyte concentrations. All experiments were performed at  $25 \pm 2$  °C, the relative experimental error is about 15%.

The flow-through reactors consisted of modified air-monitoring cassettes containing a holder for membrane filters (31). A known amount of soil material (2–10 g) was placed into each cell on a 0.45- $\mu\text{m}$  cellulose nitrate filter, and the cells were connected to a solution storage vessel and a multichannel peristaltic pump. In the first step, the soil was preconditioned in an open-loop arrangement by leaching at a rate of 3–4 mL/min with either 0.5 M  $\text{CaCl}_2$  or 1 M  $\text{NaCl}$  solutions adjusted with HCl to pH 4.6. In total, 0.5 L of electrolyte solution/g of soil was passed through the reactor cells in order to achieve complete saturation of the soil with  $\text{Ca}^{2+}$  or  $\text{Na}^+$ , respectively. The soil samples were then equilibrated with the desired  $\text{CaCl}_2$  or  $\text{NaCl}$  background electrolyte concentration adjusted to pH 4.6 in the open-loop arrangement until the effluent reached the composition of the influent solution. For measuring sorption isotherms, known amounts of the sorbate cation ( $\text{Ca}^{2+}$  or  $\text{Na}^+$ ) were added, and the soil samples were equilibrated in a closed-loop arrangement in which the electrolyte solution is recirculated through the soil material (31). The ratio between total amount of soil and electrolyte solution was varied between 2 and 1000 g/L in order to obtain fractions of the sorbate cations remaining in solution between 0.2 and 0.8; an essential prerequisite for accurate measurements of surface excess. After 24 h, the equilibrium solution was removed and analyzed for  $\text{Ca}^{2+}$  and  $\text{Na}^+$  by atomic absorption or inductively coupled plasma atomic emission spectrometry. The final pH in the equilibrium solutions was  $4.6 \pm 0.3$ . Sorbed amounts were calculated from the difference between the initial and the final concentrations in solution and were normalized to the mass of soil material.

For classical batch experiments, soil samples (2–10 g) were placed into 500-mL centrifuge bottles (polyethylene, Nalgene), and the required electrolyte solutions were added. After being shaken for several hours, the samples were centrifuged for 30 min at 4600 rpm (6000g). At high fractions of adsorbed sodium and low ionic strength, soil dispersion occurred, and it was necessary to spin the samples for 90 min at 28000 rpm ( $10^5$  g) in an ultracentrifuge to achieve complete solid–liquid separation. The supernatant was decanted and replaced by fresh preconditioning or background electrolyte solutions, respectively. The same soil-to-solution ratios for preconditioning and sorption experiments were used as described for the flow-through reactor experiments.

**Representation of Cation-Exchange Equilibria.** The classical approach of studying cation-exchange reactions involves the analysis of the mole (or charge) fraction of an adsorbed cation as a function of the corresponding fraction in solution at constant normality of dissolved cations (8, 20). Since such ion-exchange data are traditionally plotted on a linear scale, the data sets determined in many studies typically span 1 order of magnitude in concentrations.

In this study, we follow a somewhat different approach. The sorbed amount of all cations of interest is measured as a function of the solution concentrations of cations in the background electrolyte. The data are thus represented as the amount adsorbed  $q_i$  as a function of the equilibrium concentration in solution. In the present case, we measure the sorbed amount of  $\text{Ca}^{2+}$  as a function of solution concentrations of  $\text{Ca}^{2+}$  and  $\text{Na}^+$ , and the amount of sorbed  $\text{Na}^+$  is measured as a function of the same variables. Plotting the data on logarithmic scales has the further advantage that exchange data spanning over many orders of magnitude can be shown and that the behavior of the isotherms at low cation concentrations becomes clearly visible.

## Results and Discussion

**Cation Adsorption Isotherms.** Experimental sorption isotherms for both cations  $\text{Ca}^{2+}$  and  $\text{Na}^+$  to the natural

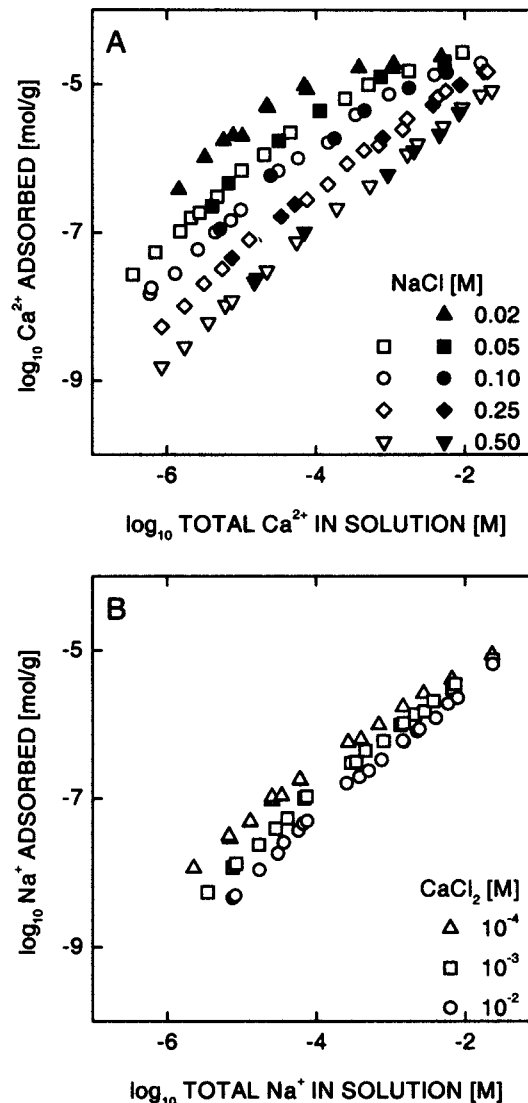


FIGURE 1. Experimental sorption isotherms for (A)  $\text{Ca}^{2+}$  in the presence of various  $\text{NaCl}$  concentrations, and (B) for  $\text{Na}^+$  in the presence of various  $\text{CaCl}_2$  concentrations in a loamy soil. The isotherms were measured by classical batch (solid symbols) and flow-through reactor (open symbols) techniques.

heterogeneous soil material presented in Figure 1 span over 4 orders of magnitude in solution concentration, which is a wide range as compared to most previously published data on the sorption of major cations in soils.

Figure 1A shows sorption isotherms for  $\text{Ca}^{2+}$  in the presence of various  $\text{NaCl}$  concentrations as background electrolyte, measured by classical batch and flow-through reactor experiments. The results obtained by both techniques are identical within experimental error. At high  $\text{Ca}^{2+}$  concentrations, the isotherms level off and reach a plateau corresponding to the cation-exchange capacity of  $5.9 \times 10^{-5}$  mol/g. For low concentrations, the data follow almost a linear isotherm. Because of cation competition, sorption of  $\text{Ca}^{2+}$  decreases with increasing  $\text{Na}^+$  background concentration. Since the competing cation,  $\text{Na}^+$ , is in excess, its solution concentration remains almost constant. The different solid–solution ratios used lead to different amounts of  $\text{Na}^+$  preadsorbed on the solid phase, which results in small point-to-point variation in the  $\text{Na}^+$  solution concentration.

Figure 1B shows  $\text{Na}^+$  sorption isotherms in the presence of various  $\text{CaCl}_2$  concentrations as background electrolyte. Again, sorption of  $\text{Na}^+$  increases with increasing  $\text{Na}^+$



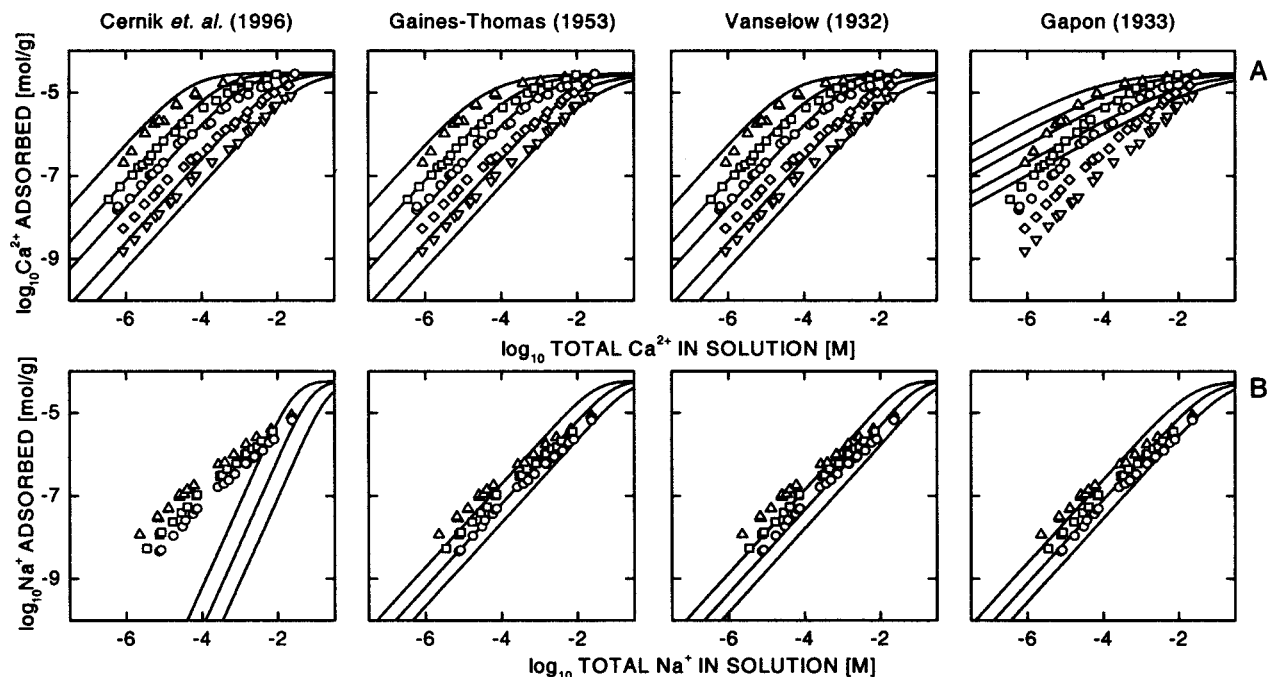


FIGURE 2. Experimental (symbols) and calculated (lines) sorption isotherms based on different cation-exchange conventions assuming a single type of cation-exchange site (one-site models). (A)  $\text{Ca}^{2+}$  sorption in the presence of various  $\text{NaCl}$  concentrations, and (B)  $\text{Na}^{+}$  sorption in the presence of various  $\text{CaCl}_2$  concentrations (see Figure 1 for legend).

concentration and decreasing  $\text{Ca}^{2+}$  concentration in solution. However, the  $\text{Na}^{+}$  sorption isotherms did not reach a plateau, indicating that the soil surfaces were never entirely saturated with  $\text{Na}^{+}$ . The presence of  $\text{Ca}^{2+}$ , which is more strongly sorbed, prevented complete  $\text{Na}^{+}$  saturation of the cation-exchange sites.

**Performance of One-Site Cation Binding Models.** Figure 2 shows a comparison of the experimental sorption data with calculated cation sorption isotherms based on the different exchange conventions assuming a single type of binding site (Table 1). Because of the wide range of concentrations and the availability of the isotherms for both cations, the comparison of different binding models with the data is straightforward. Since only a semiquantitative description of the data was possible with any of the one-site models, we do not report on least-squares fits, but we have simply selected suitable model parameters in order to obtain best data representation and facilitate comparison. For the Gaines–Thomas and Cernik equations, we choose the selectivity coefficient of  $K = 10 \text{ mol/L}$ , while for the Vanselow and Gapon equation we use  $K = 5$  and  $K^2 = 6.25 \text{ mol/L}$ , respectively. The Gaines–Thomas selectivity coefficient is comparable to previously reported values for  $\text{Ca}^{2+}$ – $\text{Na}^{+}$  exchange in soils, which are in the range of 5–13 mol/L (1, 2, 6, 32). The concentrations correspond to the respective preconditioning solutions, namely, before addition of sorbate cations to the reactor cells.

As evident from the figure, Gaines–Thomas and Vanselow conventions do provide a rather reasonable description of the data, while the Cernik and Gapon conventions fail. The Cernik convention still performs well for the  $\text{Ca}^{2+}$  data, while the Gapon convention describes the  $\text{Na}^{+}$  data reasonably well. The reason for this behavior is related to functional dependence of the isotherm at low concentrations. In the doubly logarithmic representation used here, the experimental data show approximately a slope of unity at low concentrations, which is in semiquantitative accord to the isotherms derived from the Gaines–Thomas and Vanselow conventions. However, the Cernik convention leads to an  $\text{Na}^{+}$  isotherm with a slope of 2, while the Gapon convention

leads to a  $\text{Ca}^{2+}$  isotherm with a slope of 1/2 on the log–log plot. This characteristic behavior is not easily recognized on a data set where only the sorption of a single cation over a narrow range has been measured.

A detailed analysis of the model performance shows, however, that none of the one-site models (neither with the Gaines–Thomas nor with the Vanselow conventions) is able to provide a perfect fit of the data. Both models fail in the same two respects. First, the experimentally observed dependence of the  $\text{Na}^{+}$  sorption data on the  $\text{Na}^{+}$  concentration is substantially weaker than predicted by the model (i.e., the slope is somewhat smaller than unity). Second, the  $\text{Ca}^{2+}$  sorption data depend more weakly on the  $\text{Na}^{+}$  concentration than predicted by the model. While these features are readily apparent upon closer inspection of the figures, they may not seem substantial on the doubly logarithmic plot spanning many orders of magnitude. Even when a systematic least-squares fit procedure is used, the deviations between even the best one-site model and experimental data remain substantial, and they easily exceed factors of 2–5. These deviations become obvious by calculating the root-mean-square (RMS) of the relative deviations of the model fit. The RMS of the Gaines–Thomas model is 0.93, while for the Vanselow model one obtains 1.35. These deviations are almost an order of magnitude larger than the relative experimental error, which we estimate to be around 0.15. Obviously, the one-site models are unable to model the data within experimental error.

**Multisite Cation-Exchange Models.** The agreement between the models and the experimental data improves significantly through introduction of additional types of binding sites, leading to a distribution of cation-exchange selectivities. Such multisite models represent a superposition of the cation-exchange isotherms discussed above and account for chemical heterogeneity of the soil. Figure 3A,B represents the best fit descriptions of the  $\text{Ca}^{2+}$  and  $\text{Na}^{+}$  sorption data using a multisite Cernik and multisite Gaines–Thomas model, respectively. The resulting distributions are shown in Figure 3C. For the multisite Cernik model with RMS 0.28, the description of the  $\text{Na}^{+}$  sorption data is improved

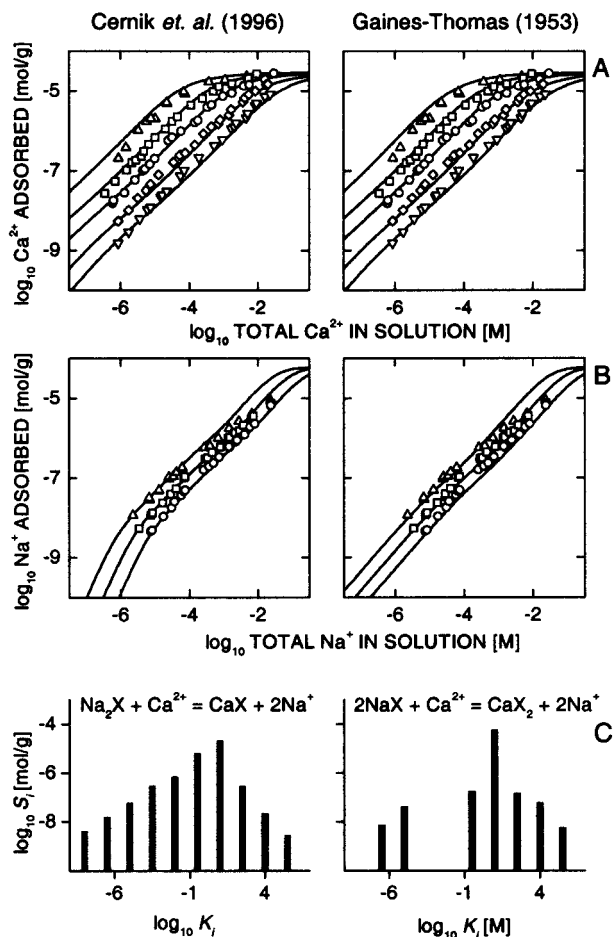


FIGURE 3. Experimental data (symbols) and multisite models (lines) based on the Cernik (left) and Gaines–Thomas (right) cation-exchange conventions. Both distributions were regularized for smoothness. (A)  $\text{Ca}^{2+}$  sorption in the presence of various NaCl concentrations, and (B)  $\text{Na}^+$  sorption in the presence of various  $\text{CaCl}_2$  concentrations (see Figure 1 for legend).

dramatically, while for the multisite Gaines–Thomas model with RMS 0.33 the description is improved to a lesser degree but still highly significantly. In both cases, the model involving distributions of exchange constants is now able to reproduce the slopes of the isotherms in the logarithmic representation well. Both conventions lead to RMS values that are now significantly lower than for any of the one-site models but still substantially larger than the experimental estimate of 0.15.

For the multisite Cernik model, the fitting procedure selects a wide distribution of exchange sites. The low-affinity sites are essential to provide a proper description of the  $\text{Na}^+$  data, while the high-affinity sites are needed for the description of the  $\text{Ca}^{2+}$  data. Despite the regularization for smoothness, a smaller number of sites results the multisite Gaines–Thomas model; the one-site Gaines–Thomas model did already provide a rather reasonable description of both  $\text{Ca}^{2+}$  and  $\text{Na}^+$  sorption isotherm data (Figure 2). Figure 3C shows the bimodal distribution of exchange constants for this model, with the majority of sites having a higher affinity for  $\text{Ca}^{2+}$  than for  $\text{Na}^+$ , but a few sites having a high  $\text{Na}^+$  affinity. These highly  $\text{Na}^+$  selective binding sites were necessary to decrease the slope of the  $\text{Na}^+$  sorption isotherms to a value slightly less than 1. The results for the Vanselow convention (not shown) are very similar to those for the Gaines–Thomas case.

All models used so far do assume an exchange ratio between  $\text{Na}^+$  and  $\text{Ca}^{2+}$  of exactly 2. The best fit of the  $\text{Ca}^{2+}$

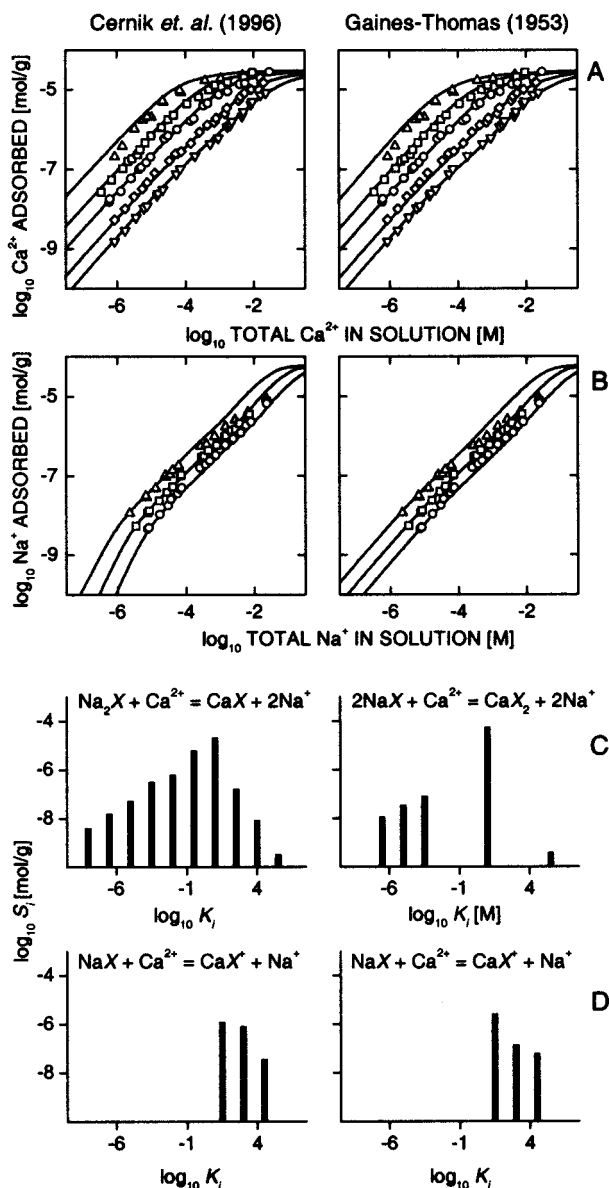


FIGURE 4. Experimental data (symbols) and multisite models (lines) based on the Cernik (left) and Gaines–Thomas (right) convention plus 1:1 exchange sites for  $\text{Ca}^{2+}$ – $\text{Na}^+$  exchange. Both distributions were regularized for smoothness. (A)  $\text{Ca}^{2+}$  sorption in the presence of various NaCl concentrations, and (B)  $\text{Na}^+$  sorption in the presence of various  $\text{CaCl}_2$  concentrations (see Figure 1 for legend).

data indicate that this exchange ratio is somewhat smaller than 2 since the model overestimates the dependence of the  $\text{Ca}^{2+}$  sorption isotherms on  $\text{Na}^+$ . This systematic discrepancy between model and experiment can be removed by allowing for 1:1 exchange sites. Figure 4 shows the fitting results for multisite Cernik and multisite Gaines–Thomas models, extended by the introduction of additional exchange sites with 1:1 stoichiometry for  $\text{Na}^+$ – $\text{Ca}^{2+}$  exchange. The distributions of 2:1 exchange constants remains nearly unchanged (Figure 4C), but a small concentration of additional sites with 1:1 stoichiometry leads to a further improvement in the fits. Note that this additional improvement, which is statistically highly significant, cannot be obtained within any model with fixed 2:1 stoichiometry.

The resulting RMS values are 0.24 for both models based on the Cernik and Gaines–Thomas conventions. Even though these values still somewhat higher than 0.15 as expected from the experiment, any further model improvements are not warranted. The model now describes the dependency of

the Ca<sup>2+</sup> sorption isotherms on Na<sup>+</sup>. The representations shown in Figures 2-4 are slightly misleading because the solid lines were calculated using the fixed background cation concentrations given in Figure 1. Small deviations from this assumption did occur for Na<sup>+</sup> sorption isotherms at the lowest Ca<sup>2+</sup> concentrations and at high Na<sup>+</sup> concentrations since the background concentration of the competing ion no longer remains constant. While the modeling takes this variation into account, it cannot be easily represented graphically. Therefore, the models reproduce the experimental data better than one would infer from Figure 4. It is interesting to realize that an excellent fit of entire data set can be achieved with two entirely different mechanisms (cf. eq 3 and eq 11). One should also note that a fit of a comparable quality cannot be achieved within the Rothmund-Kornfeld model (28), since it locks the Na<sup>+</sup>-Ca<sup>2+</sup> exchange ratio to 2.

Classical one-site cation-exchange equations according to the Gaines-Thomas and Vanselow conventions describe the sorption Na<sup>+</sup> and Ca<sup>2+</sup> to a natural soil material semiquantitatively, while other conventions fail entirely. However, none of these one-site model are able to reproduce the cation sorption data spanning a wide range in solution composition accurately. Significant improvements in the model fits were obtained by introducing a distribution of binding sites with different cation-exchange selectivities. Optimal description of the data was obtained by introducing sites with a 1:1 exchange stoichiometry for Ca<sup>2+</sup>-Na<sup>+</sup> exchange. Although the resulting distributions are strictly empirical, such multisite models are thermodynamically consistent and account for the chemical heterogeneity of the soil matrix. Such models are easily incorporated into common speciation codes and can be applied to all kinds of environmental materials. Regardless of the exact molecular mechanisms involved, such a framework is very promising to discuss more complex multicomponent situations, the effects of protons, or other types of trace ions. This key point illustrates the possibility of constructing valid models for complex materials, such as soils and sediments, without the knowledge of the actual molecular mechanisms.

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### Supporting Information Available

Tables of all experimental data points and model parameters for the multisite are included (5 pages). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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