Cation competition in a natural subsurface material: Prediction of transport behavior

V. M. Vulava,[1] R. Kretzschmar, K. Barmettler, and A. Voegelin

Department of Environmental Sciences, Swiss Federal Institute of Technology, Schlieren, Switzerland

D. Grolimund

Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland

M. Borkovec

Department of Inorganic, Analytical, and Applied Chemistry, University of Geneva, Geneva, Switzerland

[1]   Predicting the transport of reactive chemicals in subsurface porous media requires accurate adsorption models. This study compares the ability of various cation exchange models to quantitatively capture the transport behavior of major cations (i.e., calcium and sodium) in soil laboratory columns over a wide range of pore water composition. Experimental breakthrough curves were compared with model predictions without adjustable parameters. Various one-site and multisite cation exchange models were independently calibrated with batch adsorption data. Our results show that a one-site cation exchange model based on the well-known Gaines-Thomas convention yields good predictions of cation transport behavior, although some deviations from experimental data remain. The most reliable predictions were obtained with multisite cation exchange models with a distribution of various types of exchange sites.   *INDEX TERMS:* 1832 Hydrology: Groundwater transport; 1099 Geochemistry: General or miscellaneous; *KEYWORDS:* Multicomponent chromatography, affinity spectra, reactive transport, exchange conventions, exchange equilibrium

1.   Introduction

[2]   Predicting the transport of reactive chemical species in subsurface environments generally requires a chemical model coupled with an appropriate mass transport model [*Schweich and Sardin*, 1981; *Appelo*, 1994; *Bjerg et al.*, 1993; *Brusseau*, 1994; *Grant et al.*, 1995]. When several competing chemical species are present at the same time, quite complex coupled breakthrough patterns can arise [*Valocchi et al.*, 1981; *Cernik et al.*, 1994; *Wagner et al.*, 1994; *Meeussen et al.*, 1996; *Grolimund et al.*, 1996]. The prediction of transport in the presence of such competitive multicomponent phenomena is particularly sensitive to the accuracy of the underlying chemical model. One of the most important competition phenomena occurring in many soils and groundwater aquifers is the cation exchange reaction leading to multicomponent transport [*Appelo et al.*, 1990; *Gaston and Selim*, 1990; *Kohler et al.*, 1996; *Gomis-Yagües et al.*, 1997]. Examples where concentration gradients induce complex transport patterns include freshwater-seawater intrusions in aquifers, landfill contaminant plumes, and fertilization of soils with soluble salts.

[3]   Cation exchange reactions in soils and sediments are commonly described using competitive exchange models [*Stumm and Morgan*, 1996]. The most popular equations are from *Vanselow* [1932], *Gaines and Thomas* [1953], and *Gapon* [1933], while another more recent convention was proposed by *Cernik et al.* [1996]. The different cation exchange conventions have been applied to model multicomponent transport of major cations with varying success. For example, *Valocchi et al.* [1981] have modeled field data with the Gaines-Thomas convention, and the same data set was later interpreted with the Vanselow convention [*Miller and Benson*, 1983] and the Gapon convention [*van Ommen*, 1985]. Within a limited concentration range the Vanselow and Gaines-Thomas conventions provide relatively good descriptions of multicomponent transport of major cations [*Valocchi et al.*, 1981; *Appelo et al.*, 1993; *Bjerg et al.*, 1993; *Cernik et al.*, 1994; *Grant et al.*, 1995]. On the other hand, it has been shown that isotherms derived from the Gapon convention yield an unrealistically weak concentration dependence at low concentrations [*Appelo et al.*, 1993; *Vulava et al.*, 2000]. A common problem of all one-site cation exchange models is that experimental data spanning wide ranges in solution composition are not properly described with such exchange isotherms, which is sometimes interpreted as a variation of the selectivity coefficient with cation saturation of the exchanger phase [*McBride*, 1994; *Momii et al.*, 1997] or with Freundlich-like ion exchange isotherms [*Bond*, 1995]. Whether transport behavior will be predicted accurately over a wide range of concentrations in a natural subsurface material is not clear.

[4]   *Vulava et al.* [2000] have studied cation exchange equilibria between the two major cations Ca^{2+} and Na^+ in a natural soil material over wide ranges in solution composition. They demonstrated that some classical one-site cation exchange equations do not describe cation exchange isotherms over a wide concentration range correctly. Accounting for chemical heterogeneity by introducing a distribution of binding sites resulted in significant improvements of the description of cation exchange equilibria. The objective of the present study is to compare

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[1]Now at Department of Geological Sciences, University of Tennessee, Knoxville, Tennessee, USA.

various one-site and multisite cation exchange models, coupled with an appropriate mass transport model, in their ability to predict the transport behavior of Ca^{2+} and Na^+ in laboratory soil columns without any adjustable parameters over a wide compositional range.

2. Materials and Methods

2.1. Soil Material

[5] The soil material used for cation exchange and column experiments was collected from the B horizon of a noncalcareous, acidic soil in northern Switzerland (Riedhof soil, dystric Eutrochrept). The soil material was dried at 40°C, gently crushed, and passed through a 2-mm sieve. For column experiments an aggregate size fraction between 63 and 400 μm 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 H_2O), and a cation exchange capacity of 5.9×10^{-5} mol/g. X-ray diffraction analysis showed that the soil contained quartz, vermiculite, illite, kaolinite, chlorite, and goethite.

2.2. Column Transport Experiments

[6] Dry soil aggregates were packed into two different glass chromatography columns (Omnifit, Cambridge, England). In order to facilitate saturation with water the packed columns were initially purged for 5 min with CO_2 gas. They were then water-saturated by pumping a 0.5-M $CaCl_2$ solution through a degasser and through the column in the upward direction at a rate of 0.1–0.3 mL/min. To saturate the cation exchange sites of the soil with Ca^{2+}, at least 200 pore volumes of 0.5-M $CaCl_2$ solution were passed through the soil columns. The electrolyte concentration was then reduced to 0.01 M $CaCl_2$ for tracer pulse experiments and further adjusted to the desired values for cation breakthrough experiments.

[7] Pore volume and column Peclet number were determined by short-pulse tracer breakthrough experiments. Pulses of electrolyte solutions containing 1 to 10 mM NO_3^- as a conservative tracer were injected using a 0.1-mL injection loop and the NO_3^- concentration in the effluent was monitored on-line using a flow-through UV-visible light spectrometer set to a wavelength of 220 nm. By comparing its breakthrough with Br^- and ClO_4^- in similar soil materials we found identical breakthrough curves and thus verified that NO_3^- represents a conservative tracer. From first and second moments of the NO_3^- breakthrough curve the average travel time of the tracer and its dispersivity were calculated according to standard procedures [*Villermaux*, 1981; *Bürgisser et al.*, 1993].

[8] Four transport experiments were conducted to test the cation exchange and transport models over a wide range of solution composition. The sequences of input solutions for each experiment are summarized in Table 1. The effluent was collected in a fraction collector, acidified with suprapure HNO_3 to pH < 2, and analyzed for Na^+ and Ca^{2+} either by atomic absorption spectrometry (Varian SpectrAA 400) or by inductively coupled plasma-atomic emission spectrometry (Varian Liberty 400) equipped with an ultrasonic nebulizer (Cetac U-5000 AT).

[9] The experiments were carried out in two different soil columns. For experiments 1, 2, and 4 (see Table 1) the column was 50 cm long and had a 0.3-cm inner diameter. The pore volume was 2.1 mL, and its Peclet number was $Pe \approx 200$. For experiment 3 (see Table 1) the column was 12 cm long and had a 1.0-cm inner diameter. Its pore volume was 5.6 mL, and its Peclet number was $Pe \approx 50$. The resulting flow velocities were in the range of (2–4)

**Table 1.** Concentrations of Ca^{2+} and Na^+ in the Influent Solutions Used in the Four Transport Experiments

Pore Volume[a]	Ca^{2+}, mM	Na^+, mM
Experiment 1		
<0	4.47	105
0	7.70	0.00
14	0.00	98
Experiment 2		
<0	1.00	0.00
0	1.04	1.22
10	1.10	11.70
25	1.00	0.113
Experiment 3		
<0	0.40	100
0	0.40	520
20	0.31	102
90	0.40	255
120	0.38	102
180	0.39	56
250	0.38	255
275	0.39	56
355	0.40	530
375	0.38	56
Experiment 4		
<0	0.1075	231
0	1.0000	53
10	0.0105	101
30	0.0015	520

[a] Values given for pore volumes <0 represent the concentrations in the preconditioning solutions.

$\times 10^{-4}$ m/s, and the resulting dispersivities were around 2.5 mm. In both columns the packing density, defined as dry mass per unit pore volume, was 1.93 ± 0.05 g/mL.

2.3. Transport Modeling

[10] The breakthrough curves of Ca^{2+} and Na^+ were predicted using a standard mixing cell transport model coupled to chemical equilibrium reactions. The calculations were carried out with the computer code IMPACT [*Jauzein et al.*, 1989]. The mixing cell model provides an excellent approximation of the convection-dispersion equation, provided that the column Peclet number Pe > 50. This number is given by $Pe = J/2$, where J is number of mixing cells [*Villermaux*, 1981]. In the calculations we have used $Pe = 50$. The adsorption reactions were modeled by one-site and multisite Cernik and Gaines-Thomas cation exchange models, respectively. In the Gaines-Thomas convention the heterovalent exchange between Ca^{2+} and Na^+ is written as

$$2Na X + Ca^{2+} \leftrightarrow Ca X_2 + 2Na^+, \qquad (1)$$
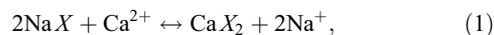
where X is a surface site of charge -1. In this case, the total site concentration per unit mass of the solid S equals the cation exchange capacity Q (in moles of charge per unit mass of sorbent). In the cation exchange convention proposed by *Cernik et al.* [1996], the reaction is written as

$$Na_2 Y + Ca^{2+} \leftrightarrow CaY + 2Na^+, \qquad (2)$$
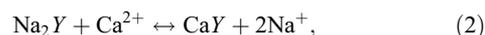
where Y now denotes a site of charge -2. In this case, the total site concentration S is related to the cation exchange capacity Q by $S = Q/2$. In order to allow for a noninteger exchange ratio between

Table 2. Model Parameters for One-site and Multisite Cernik et al. and Gaines-Thomas Cation Exchange Models Used in Transport Predictions[a]

	Exchange Site Ratio	$\log K_i$, mol/L[b]	$\log S_i$, mol/g
One-site Cernik et al. model	1:2	1.0	−4.53
One-site Gaines-Thomas model	1:2	1.0	−4.23
Multisite Cernik et al. model	1:2	−8.0	−8.39
		−6.5	−7.81
		−5.0	−7.23
		−3.5	−6.52
		−2.0	−6.15
		−0.5	−5.20
		1.0	−4.67
		2.5	−6.54
		4.0	−7.66
		5.5	−8.55
Multisite Gaines-Thomas model	1:2	−6.5	−8.14
		−5.0	−7.39
		−0.5	−6.76
		1.0	−4.24
		2.5	−6.84
		4.0	−7.23
		5.5	−8.25
Multisite Cernik et al. model	1:2 and 1:1	−8.0	−8.40
		−6.5	−7.82
		−5.0	−7.30
		−3.5	−6.52
	1:2	−2.0	−6.22
		−0.5	−5.21
		1.0	−4.68
		2.5	−6.80
		4.0	−8.09
		5.5	−9.50
		1.5	−5.93
	1:1	3.0	−6.09
		4.5	−7.45
Multisite Gaines-Thomas model	1:2 and 1:1	−6.5	−7.95

[a] From *Vulava et al.* [2000].
[b] K_i for 1:1 exchange sites is dimensionless.

Ca^{2+} and Na^+ we also considered an additional 1:1 exchange reaction involving protons

$$NaHZ + Ca^{2+} \leftrightarrow CaZ + Na^+ + H^+, \qquad (3)$$
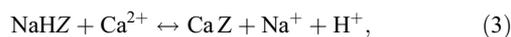
where Z denotes a site of charge −2. Here the total site concentration is again related to the cation exchange capacity Q by $S = Q/2$. Because of the low concentration of protons we do not consider effects of pH in this study and simply model this reaction as 1:1 exchange between Ca^{2+} and Na^+ [*Vulava et al.*, 2000]. It must be noted that this reaction alone is not sufficient to capture the effects of pH during the breakthrough.

[11] The mass action laws and corresponding adsorption isotherm equations for Ca^{2+} and Na^+ were derived under the assumption that the activities of adsorbed cations correspond to their equivalent fractions on the exchanger phase [*Vulava et al.*, 2000]. The activity coefficients for dissolved species were calculated using the Davies equation [*Stumm and Morgan*, 1996]. Ion pair formation in solution was taken into account, but adsorption of chloride complexes to the soil matrix was assumed to be negligible.

[12] When a single type of exchange site was used, we refer to a one-site model. On the other hand, multisite models consist of several types of exchange sites with different exchange selectivity coefficients, leading to a linear superposition of exchange isotherms. Multisite models were previously used to model adsorption to natural materials [*Westall et al.*, 1995; *Cernik et al.*, 1996;

Kohler et al., 1996]. In both cases, we use either the *Gaines and Thomas* [1953] or the *Cernik et al.* [1996] convention for defining the exchange reaction between Ca^{2+} and Na^+ with exchange stoichiometry of 1:2. We also consider models where 1:1 exchange sites equation (3) are used in addition to the 1:2 sites. The different models were calibrated by least squares fit to an extensive data set of competitive adsorption data, on the basis of methods described elsewhere [*Cernik et al.*, 1995, 1996]. The various models and corresponding parameters used are summarized in Table 2. All one-site and multisite models were calibrated independently with batch adsorption data [*Vulava et al.*, 2000], and therefore the transport predictions do not contain any adjustable parameters.

3. Results and Discussion

3.1. Performance of One-Site Models

[13] The results of the first column experiment showing the coupled breakthrough of Na^+ and Ca^{2+} through laboratory soil columns are presented in Figure 1 (see also Table 1). The symbols are experimental data, and lines represent the corresponding transport predictions based on one-site isotherm equations derived from the *Gaines and Thomas* [1953] and *Cernik et al.* [1996] cation exchange conventions given in equations (1) and (2), respectively.
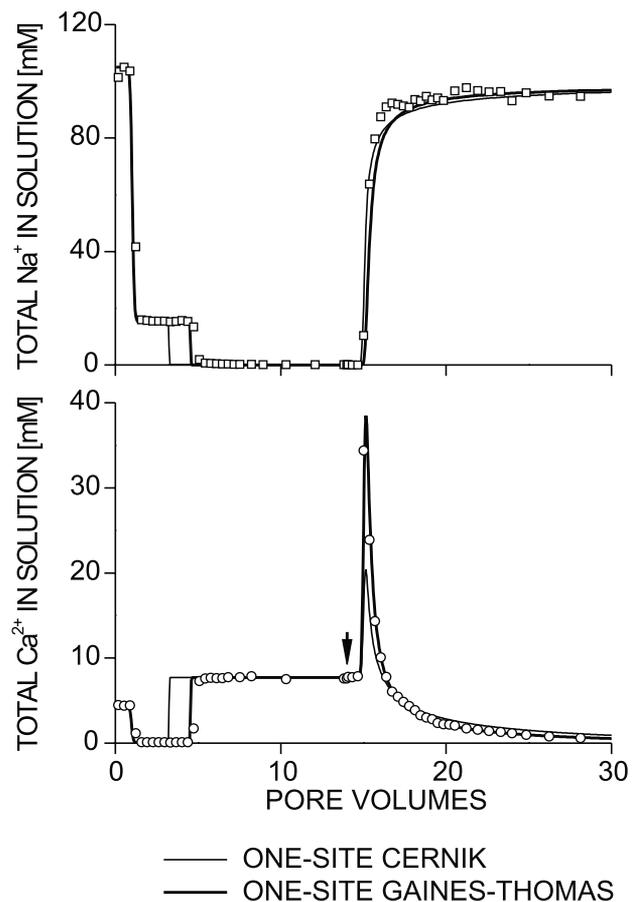

——— ONE-SITE CERNIK
——— ONE-SITE GAINES-THOMAS

Figure 1. Breakthrough curves of Ca^{2+} and Na^+ through a packed soil column as a result of changes in feed solution composition (see Table 1, experiment 1) at 0 and 14 pore volumes (arrow). Lines represent model predictions based on two different one-site cation exchange models. Note that each change in feed solution results in a nonretarded normality front and a retarded cation exchange front.
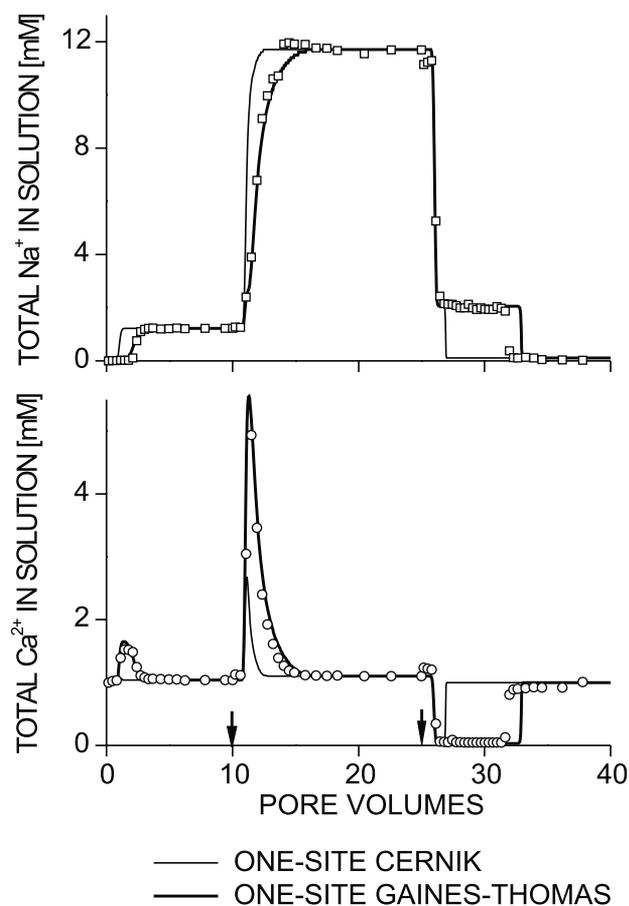
Figure 2. Breakthrough curves of Ca^{2+} and Na^+ through a packed soil column as a result of changes in feed solution Na^+ concentration at 0, 10, and 25 pore volumes (arrows). The Ca^{2+} concentration in the influent was kept constant at 1 mM (see Table 1, experiment 2). Lines represent model predictions based on two different one-site cation exchange models.

The column was pre-conditioned with a solution containing both Ca^{2+} and Na^+. At time zero the influent was switched to a solution containing only Ca^{2+} (Table 1). This change in feed solution resulted in two well-separated fronts. The first front is a so-called "normality front," which moves through the porous medium unretarded and therefore appears in the column effluent after exactly one pore volume. It reflects the change in total normality of the input solution. Since Na^+ has a lower affinity to the exchange sites than Ca^{2+}, and the concentration of Na^+ decreases, the second front is self-sharpening, where Ca^{2+} replaces adsorbed Na^+ from the exchange sites in the soil matrix. This front appeared after ~5 pore volumes (Figure 1). The second change in feed solution was induced after 14 pore volumes, when the influent was switched to a solution of higher normality containing only Na^+. Again two fronts are observed, although they cannot be completely separated because of dispersion. The first front is the unretarded normality front resulting in a sharp increase in Ca^{2+} concentration in the effluent at exactly 15 pore volumes. The second front is the retarded cation exchange front in which Na^+ replaces adsorbed Ca^{2+} from the cation exchange sites. Since Na^+ has a lower affinity to the exchange sites than Ca^{2+}, and the concentration of Na^+ increases, this front is self-broadening and results in a continuous decrease of the Ca^{2+} concentration and a corresponding increase of the Na^+ concentration in the column effluent. This behavior is well

known in the theory of nonlinear chromatography [*Schweich and Sardin*, 1981].

[14] For this experiment both one-site cation exchange models in combination with the mixing cell transport model provided accurate predictions of the unretarded normality fronts at 1 and 15 pore volumes. However, the position of the retarded Ca^{2+} for Na^+ exchange front (at 5 pore volumes) was predicted correctly only by the Gaines-Thomas model. Since in this experiment the second feed solution contained only Ca^{2+}, the position of this exchange front depends on the initial amount of Na^+ adsorbed to the soil matrix. The one-site Cernik model underestimated the amount of Na^+ adsorbed, which is consistent with the poor fit of this model to batch Na^+ adsorption data [*Vulava et al.*, 2000]. The self-broadening cation exchange front (at 15–30 pore volumes) was predicted reasonably well with both models.

[15] Experiment 2 on the same system is shown in Figure 2 (see also Table 1). Here the column was preconditioned with a 1 mM $CaCl_2$ solution. The Ca^{2+} concentration in the influent was kept constant at ~1 mM throughout the entire experiment. The Na^+ concentration in the feed solution was changed three times during the experiment, resulting in positive or negative changes in effluent
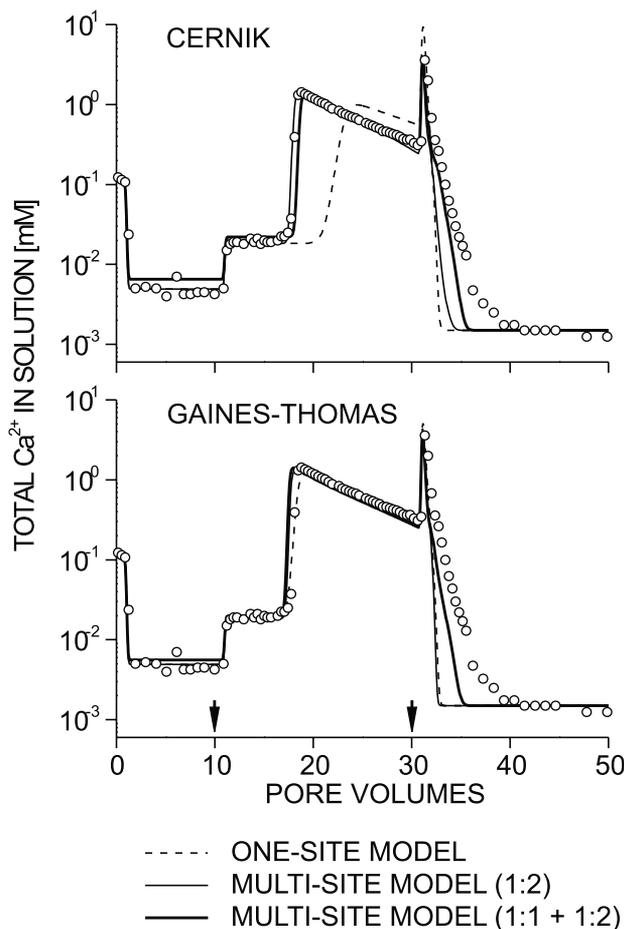

Figure 3. Effluent concentrations of Ca^{2+} from a packed soil column as a result of changes in feed solution Ca^{2+} and Na^+ concentrations (see Table 1, experiment 4) at 0, 10, and 30 pore volumes (arrows). Dashed lines represent model predictions based on one-site cation exchange models, whereas solid lines represent predictions based on multisite cation exchange models with either 1:2 exchange stoichiometry or a combination of 1:2 and 1:1 exchange sites.
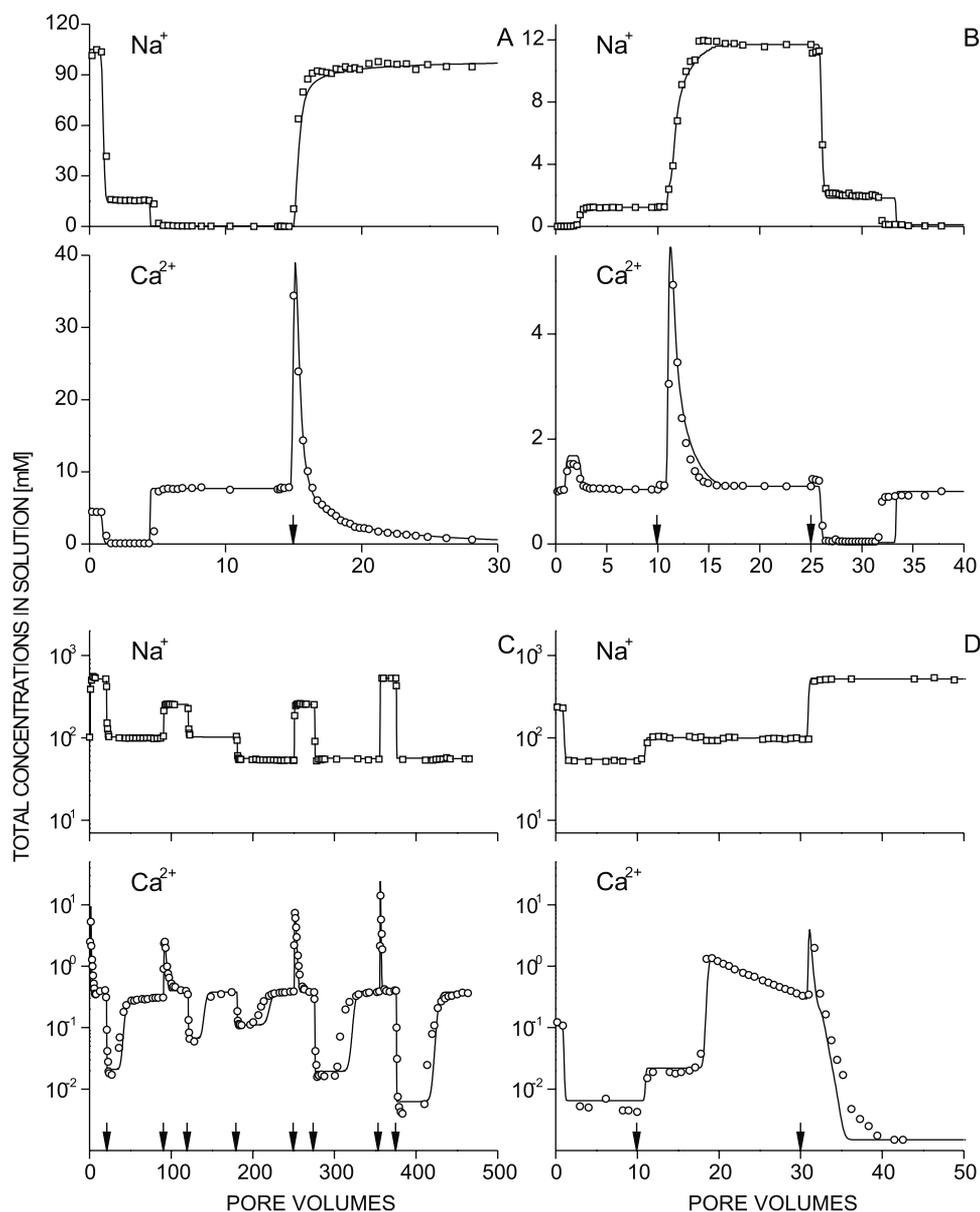
Figure 4. Summary of all four column breakthrough experiments and corresponding predictions based on a multisite Cernik cation exchange model with 1:2 and 1:1 stoichiometry exchange sites (lines): (a) experiment 1, (b) experiment 2, (c) experiment 3, and (d) experiment 4. With few exceptions, excellent predictions were achieved for all four experiments covering wide ranges in solution composition.

Ca^{2+} concentration. Again, clear differences can be observed between the model predictions based on one-site Cernik and Gaines-Thomas models. The one-site Gaines-Thomas model again provided an excellent prediction of the breakthrough curves, except for the last exchange front at 32 pore volumes. In contrast, the one-site Cernik model resulted in an inferior prediction of the Ca^{2+} and Na^+ breakthrough curves, which is consistent with the insufficient performance of this model in describing Na^+ adsorption isotherms in the presence of Ca^{2+} [*Vulava et al.*, 2000].

[16] Figure 3 shows the results of experiment 4 (see also Table 1), in which the Ca^{2+} and Na^+ concentrations in the input solution were varied independently. In contrast to previous experiments, changes in solution composition were induced before the overall equilibrium in the column was established. Hence the fronts occurring in this experiment do overlap, an aspect which further complicates the breakthrough pattern of Na^+ and Ca^{2+}. The Ca^{2+} concentration measured in the column effluent in this experiment is depicted in Figure 3. The effluent concentration is now plotted on a logarithmic scale, ensuring better visibility of changes in the lower concentration range. The one-site Cernik cation exchange model again resulted in large discrepancies between predicted and experimental Ca^{2+} breakthrough curves. The one-site model based on the Gaines-Thomas convention performed much better, but deviations from the experimental data still remain for the last exchange front (at 32–40 pore volumes), where the experimental data exhibit a long tailing, while the one-site models predict a sharp decrease in Ca^{2+} concentration.

[17] In spite of the complexity of the material used, the simple one-site Gaines-Thomas model performs astonishingly well. While some systematic deviations remain, the Gaines-Thomas model is capable of predicting transport behavior over a wide

range of concentrations surprisingly well given its simplicity (see Figures 1, 2, and 3). The one-site Cernik model performs substantially worse. The Vanselow model was not tested in detail but is expected to perform very similarly to the Gaines-Thomas model [*Vulava et al.*, 2000]. As will be shown in section 3.2, the performance of both models can be improved by introducing a distribution of exchange sites.

3.2.   Performance of Multisite Models

[18]   The solid lines in Figure 3 represent predictions of transport behavior which are based on four different multisite models using the Cernik and Gaines-Thomas cation exchange conventions with and without introduction of additional 1:1 stoichiometry exchange sites, respectively. When the Cernik convention was used to define the multisite cation exchange model, additional types of exchange sites resulted in significant improvements in the model fit to batch adsorption data, particularly for Na^+ adsorption experiments. The best fit of batch adsorption data was achieved if additional 1:1 sites were included in the model, allowing for an overall non-stoichiometric exchange [*Vulava et al.*, 2000]. Figure 3 shows that the multisite Cernik models also provide a much better prediction of transport. Introducing additional 1:1 exchange sites particularly improved the prediction of the last diffuse cation exchange front between 32 and 40 pore volumes.

[19]   When the Gaines-Thomas model was used to define a multisite cation exchange model, additional types of 1:2 exchange sites did not significantly improve the transport predictions (Figure 3). Only the introduction of 1:1 exchange sites resulted in an improved prediction of the last diffuse cation exchange front.

[20]   The overall performance of the multisite 1:2 and 1:1 Cernik model with all four transport experiments is presented in Figure 4. With few exceptions, this model yields excellent predictions of the coupled transport of Ca^{2+} and Na^+ in soil columns, which can be considered physically uniform but chemically heterogeneous (at the molecular level). Basically identical predictions (not shown here) are obtained with a multisite 1:2 and 1:1 Gaines-Thomas cation exchange model. We suspect that with such multisite models based on other conventions could be successfully used to obtain very similar predictions of the transport behavior, for example, with the Vanselow model.

[21]   Note that only in the last diffuse cation exchange front of experiment 4 does the multisite model show a substantial improvement over the simple one-site Gaines-Thomas model. The one-site Gaines-Thomas model predicts experiments 1–3 equally well.

4.   Conclusion

[22]   Various cation exchange models were compared for their ability to predict the transport behavior of major cations (Ca^{2+}, Na^+) in soil laboratory columns over a wide composition range. Various one-site and multisite cation exchange models were independently calibrated with batch adsorption data, and thus the transport predictions do not contain any adjustable parameters. Our results show that a one-site cation exchange model based on the well-known Gaines-Thomas convention yields very good predictions of cation transport behavior, although some deviations from experimental data remain. The predictions were improved for multisite cation exchange models with a distribution of various types of exchange sites.

[23]   The simulation results are rather insensitive to the dispersion characteristics of the column (i.e., precise value of the Peclet number). This observation applies since the Peclet number is rather high and the column experiments were carried out over several tenths of pore volumes. The spreading of the (retarded) self-broadening fronts originates from the nonlinearity of the adsorption isotherms, and the shape of the fronts is basically unaffected by dispersion. Dispersion of the medium merely affects the precise shape of the (unretarded) normality fronts or the (retarded) sharp fronts. These fronts are very narrow on the scale of the experiment and could not be resolved. Dispersion effects would be more prominent in a spatially heterogeneous field-scale setting, however.

[24]   An important result of this study is that the transport behavior can be predicted correctly by models which are based on fundamentally different chemical mechanisms (e.g., Gaines-Thomas versus Cernik). The key requirement is that the adsorption model properly describes the multicomponent adsorption isotherms. This requirement can be achieved with both models by choosing the appropriate distribution of exchange sites. Successful predictions of transport behavior critically depend on the accurate knowledge of the adsorption isotherms for all relevant ions over a wide range of pore water concentrations, while the molecular mechanism of the adsorption reactions appears to be less important. Therefore the measurement of multicomponent adsorption data in soils or sediments represents a foremost research priority. Additional molecular information is needed, however, not only to gain a fundamental understanding of the adsorption reactions of soils and sediments but also to approach multicomponent situations where competition of many different ions becomes important.

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K. Barmettler, R. Kretzschmar, and A. Voegelin, Department of Environmental Sciences, Swiss Federal Institute of Technology, Grabenstrasse 3, CH-8952 Schlieren-Zurich, Switzerland. (barmett@ito.umnw. ethz.ch; kretzschmar@ito.umnw.ethz.ch; voegelin@ito.umnw.ethz.ch)

M. Borkovec, Department of Inorganic, Analytical, and Applied Chemistry, University of Geneva, Sciences II, 30, Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland. (michal.borkovec@cabe.unige.ch)

D. Grolimund, Swiss Light Source, Paul Scherrer Institute, CH-5232 Villigen, Switzerland. (daniel.gromilund@psi.ch)

V. M. Vulava, Department of Geological Sciences, University of Tennessee, 1412 Circle Drive, Knoxville, TN 37996-1410, USA. (vulava@ utk.edu)