Predicting multicomponent transport of cations in natural porous media

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Competitive sorption and transport of cations plays a key role in soil fertility, contaminant displacement, and colloid mobilization in soils and sediments. Understanding the movement of cations in heterogeneous, natural porous media is, therefore, of great importance. Typically, many different cations are present in such systems and they compete with each other for binding sites. Competitive cation binding can lead to quite complex transport phenomena in such multicomponent systems.

Our objective was to investigate the competitive binding of three major cations (Ca^{2+}, Mg^{2+}, and Na^{+}) in a natural soil material and to predict multicomponent transport from competitive binary and ternary adsorption isotherms. Various single-site and multiple-site models based on competitive Langmuir or cation exchange equations were tested.

Materials and methods

Cation adsorption to a non-calcareous soil (B-horizon, Riedhof soil, Switzerland) was measured using the flow-through reactor technique described by Grolimund *et al.* (1995). Binary adsorption isotherms in Ca^{2+}-Na^{+}, Mg^{2+}-Na^{+}, and Mg^{2+}-Ca^{2+} systems were measured at pH 4.5 ± 0.2. Solute concentrations ranged between $10^{-7}-10^{-1}$ M while background electrolyte concentrations ranged between 0.02–0.5 M for NaCl and $10^{-4}-10^{-2}$ M for $CaCl_2$ and $MgCl_2$. Ternary adsorption isotherms for Mg^{2+} were also measured in mixed NaCl-$CaCl_2$ background electrolytes. All cation concentrations in equilibrium solutions were measured by atomic absorption spectroscopy.

Transport experiments were performed in glass chromatography columns packed with soil material. Pore volume and dispersivity of the columns were determined from tracer breakthrough experiments (Bürgisser *et al.*, 1993). Typically, the packed soil columns used had Péclet numbers greater than 200. In cation breakthrough experiments, sequences of feed solutions of varying composition were passed through the soil columns at constant flow velocity and the cation concentrations were monitored in the column effluent.

The cation adsorption data were modeled using various single-site and multiple-site models. The local binding isotherms for each site were either based on competitive Langmuir or cation exchange equations (e.g. Gaines-Thomas). A non-linear least squares procedure was applied to obtain best-fit parameters for each model (Cernik *et al.*, 1996). The resulting adsorption models were then used to predict multicomponent transport of Ca^{2+}, Mg^{2+}, and Na^{+} in soil columns. The transport calculations were performed using a mixing-cell model, as implemented in the computer code IMPACT (Jauzein *et al.*, 1989). The ability of various adsorption models in predicting multicomponent transport was compared.

Results and discussion

The cations Ca^{2+}, Mg^{2+}, and Na^{+} displayed strong competition for binding to the soil material. It was found that the affinity of the cations to the soil material decreases in the order $Ca^{2+}>Mg^{2+}>Na^{+}$. Adsorption models based on a single adsorption site proved to be inadequate for modelling the data. Multi-site adsorption models provided a much better description of competitive cation binding data spanning over several orders of magnitude in concentration.

An example for a multicomponent transport experiment is shown in Fig. 1. Here, a laboratory soil column was pre-equilibrated with a salt solution containing 4.6, 5.3, and 4.5 mM of NaCl, $CaCl_2$, and $MgCl_2$ respectively. At time zero, the feed is switched to a solution containing only 5.3 mM $CaCl_2$. Three fronts can be observed as a result of this change in feed solution. Firstly, an unretarded normality front appears after one pore volume,

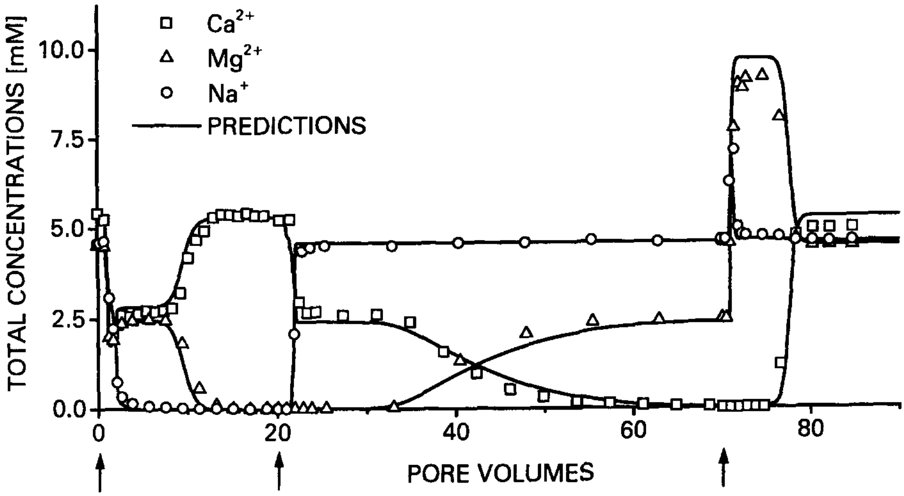

FIG. 1. Multicomponent transport of Ca^{2+}, Mg^{2+}, and Na^{+} in a soil column. The arrows indicate changes of the feed solution. The solid lines represent a prediction based on a multi-site cation exchange model.

resulting in a sharp drop in all cation concentrations. Secondly, a slightly retarded Ca^{2+} and Mg^{2+} for Na^{+} exchange front appears after approximately two pore volumes. And finally, a Ca^{2+} for Mg^{2+} exchange front is observed after about 10 pore volumes, after which the effluent reaches the composition of the feed solution.

At 20 pore volumes, the feed is switched to a solution containing 4.6 mM NaCl and 2.4 mM $MgCl_2$, thus maintaining the normality of the previous feed solution. As a result, two fronts are observed. The first is the Na^{+} for Ca^{2+} exchange front, which again is only slightly retarded. At about 40 pore volumes, the Mg^{2+} for Ca^{2+} exchange front is observed. Note, that this front is much broader than the Ca^{2+} for Mg^{2+} exchange at 10 pore volumes. The broadening of the front is due to the lower affinity of Mg^{2+} for binding sites compared to Ca^{2+}.

Finally, after 70 pore volumes the input solution is switched back to the pre-equilibration solution. Again, three fronts develop: an unretarded nomality front, a slightly retarded Ca^{2+} and Mg^{2+} for Na^{+} front, and a more strongly retarded Ca^{2+} for Mg^{2+} exchange front.

The solid lines in Fig. 1 represent a model prediction of the breakthrough curves using a multi-site adsorption model based on cation exchange equations. In this case, the model was calibrated against adsorption data for the binary cation systems only. It is evident, that the model provides an accurate prediction of all features of the breakthrough curves. The column Péclet number was the only adjustable parameter.

In conclusion, there are two main requirements for quantitative predictions of multicomponent cation transport: (i) high quality competitive adsorption data spanning over wide concentration ranges, and (ii) binding model that accurately describe the entire set of competitive adsorption data.

References

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