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Technical Article

Modeling Sorption and Exchange Processes in Column Experiments and Large Scale Field Studies

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Abstract. This paper demonstrates the possibilities of reactive transport modeling in predicting contaminant transport processes of laboratory and field scales. Basic approaches of reactive transport modeling are discussed, focusing on the incorporation of a thermodynamic description of chemical interactions into the convection-dispersion equation (CDE). Both equilibrium and kinetic approaches are presented. Chemical reaction parameters can be estimated from 1-D column experiments, by combining the CDE and the thermodynamic description of transport. A 2-D simulation with a heterogeneous flow field and ion exchange parameters obtained from column experiments is presented. The results of the 2-D model are in qualitative agreement with measured field breakthrough curves. Limitations of this approach are discussed, focusing on parameter heterogeneity and scaling effects.

Key words: Column experiments, field test, ion exchange, reactive solute transport, sorption

Introduction

Environmental impacts from mining and associated waste occur in many ways. A major problem is the pollution of water caused by these wastes or by seepage from abandoned mines and other contaminated land. The chemistry of mine lakes, seepage water, and groundwater has been studied for more than 30 years. Among the major problems are the presence of heavy metals in combination with acid mine drainage (AMD). Concentrations of dissolved metals in such mine waters are often very high. Examples can be found for a wide range of different metals like lead (Sanches et al. 1998), copper (Montero et al. 1994), iron (Bain et al. 2000; Bangthanh et al. 1999), and uranium (Nitzsche and Merkel 1999, Meinrath et al. 1999).

In order to assess the risk of groundwater contamination from AMD, it is necessary to accurately model the water flow and contaminant transport. The chemical composition of groundwater is often a complex mixture of different species. As the groundwater migrates through the porous media, the composition may be changed due to interactions with the solid matrix. Surface complexation reactions (Davis et al. 1998), ion exchange processes (Selim et al.1987), and precipitation and dissolution (Appelo 1994) due to changing pH conditions change the solution composition. Therefore, a contaminant transport model must be able to simulate the important chemical reaction processes as well as the processes of advection and dispersion. Prognosis by reactive transport simulations has become a widely accepted tool. The rapid increase of available computing power has further stimulated this development. Deep disposal of nuclear wastes and remediation procedures for sites contaminated by uranium mining activities are examples where reactive transport modeling plays an essential role in performance assessment (Helton 1994)

One of the major problems, however, is the identification of the underlying mechanisms and the estimation of the parameters in the mathematical models describing the solid-fluid interactions. In addition, the identification of these mechanisms is obscured by the natural heterogeneity of aquifer systems in terms of physical and chemical properties (Thorbjarnarson and MacKay 1994; Vereecken et al. 2000) and by the large uncertainty of the measurement and parameter prediction methods (Meinrath et al. 2000).

Solute-solid interactions

Sorption isotherms are often used to describe interactions between solutes and solid matrix. A very simple approach is based on a partition coefficient K_d, which describes a linear distribution of concentration between the solute and the solid phase in a chemical equilibrium, according to:

$$c_s = K_d c_w \qquad (1),$$

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where c_s is the concentration on the solid phase (sorbed mass per volume of water in the pore space), and c_w is the solute concentration. This simple approach is not able to describe experimental results over a wide range of concentrations. However, it is frequently used because the K_d parameter is easily determined by batch experiments and data are available. Furthermore, a linear sorption isotherm can be incorporated directly into a convection-dispersion equation (CDE) to describe reactive transport behavior. One way to extend the K_d concept to more complex interactions is by using K_d values that depend on chemical parameters like pH or organic content (Gaston and Locke 1994).

Many substances are known to undergo a more complex sorption, which may be described by nonlinear sorption isotherms like Langmuir

$$c_s = \frac{k_1 c_w}{1 + k_2 c_c} \qquad (2)$$

or Freundlich:

$$c_s = k\, c_w{}^n \qquad (3)$$

or a combination of both (Ajwa and Tabatabai 1997; Vereecken et al. 1999), where k, k_1, k_2, and n are empirical parameters that must be determined from sorption or solute transport experiments.

Another approach to describe interactions of solutes with the solid phase is based on a thermodynamic description of the reactions (e.g., the PHREEQC model, Parkhurst and Appelo 1999). The classical way to incorporate that approach is to calculate the chemical reaction term separately from the transport part for each time step and for all solute components (for instance, Walter et al. 1994). It considers dissociation, precipitation, and disolution of minerals as well as cation exchange and surface complexation. The processes can be described either as equilibrium reactions or with kinetic rates (Stumm and Morgan 1996).

The mathematical approach of PHREEQC ion exchange in equilibrium is the same as for mineral reaction using an exchanger X. The ion exchange of a cation Me^{n+} is described by the following half reaction:

$$Me^{n+} + nX^- \Leftrightarrow MeX_n \qquad (4)$$

with:

$$K_{Me} = \frac{[MeX_n]}{[Me^{n+}][X^-]^n} \qquad (5)$$

where X^- is the negatively charged ion exchanger. The brackets stand for the activity of the species both in solution and on exchange sites. The equivalent fraction is used for calculating the activity of exchangeable species (Gaines and Thomas 1953) while for solute ions, the activity is calculated from the concentration c_i with the Davies equation. The total molality of X^- is equal to the cation exchange capacity (CEC) recalculated to 1 L of pore water.

In order to include kinetic effects, the PHREEQC approach was extended. A description, based on the Bunzl rate law (Bunzl 1971; Sposito 1994) is used, which calculates the reaction amount q for solute i in a time step Δt as:

$$q_i = (c_i - c_{i,equ})e^{k\Delta t} \qquad (6)$$

(Jury and Flühler 1992), where *k* is a 1st order kinetic parameter. This rate parameter may differ for forward and backward reactions (k_f and k_b, Sposito 1994).

Water flow and solute transport

Water flow can be calculated with the TRACE model (Seidemann 1997). This model solves the Richards equation for saturated and unsaturated media using a finite element approach. Using an equal-sized decomposition of the domain and a parallel Conjugated Gradient solver, this code can be run on the CRAY T3E supercomputer.

Stationary or time-dependant velocity fields and saturation distributions can be used for the PARTRACE transport code (Neuendorf 1997). This code uses a particle tracking approach to simulate distributions, which is equivalent to solving the CDE. The PHREEQC model was incorporated into the PARTRACE code to describe chemical interactions (Nitzsche et al. 2001). The coupling is done by a sequential non-iterative approach. Chemical reactions are calculated for each element independently. The parallelization of PARTRACE is achieved by distributing the particles (up to 10^9) and the chemical interaction calculations onto different computing nodes. Elements are distributed periodically over the computing nodes so one can get a good load balancing in a static way (for both point and extended sources). Both codes were run in parallel on a CRAY T3E supercomputer. Computing times for 2-D and 3-D problems of a few hours were therefore possible, which makes it possible to use Monte Carlo approaches to model data uncertainties (Nitzsche et al. 2000).

Results and Discussion

Breakthrough curve experiments with aquifer materials

These experiments were motivated by large-scale tracer experiments conducted with lithium chloride in an unconfined aquifer at the Krauthausen field site (Vereecken et al. 2000). Lithium was used as a tracer because, to some extent, it simulates the behavior of heavy metals. However, lithium does not react with organic matter or minerals in the same manner as many heavy metals; also, ion exchange is not as strong as it is for most of the heavy metals. This leads to acceptable experimental times. Lithium can be used as a tracer in the natural environment without endangering groundwater quality.

To demonstrate the application of the combined solute transport modeling with the extended PHREEQC model, we used breakthrough curves (BTCs) from solute displacement studies with LiBr, NaBr and $MgBr_2$. Aquifer material was collected at the Krauthausen test site at a depth between 9 and 10 m. These experiments were conducted in the framework of a large scale tracer experiment to elucidate the basic mechanisms of the lithium interactions with the solid phase. Two columns (30 cm in height, 5 cm in diameter) were packed with oven-dried sediment material (<2mm). The columns were continuously leached with a $CaCl_2$ solution (approximately $0.9*10^{-3}$M) during the whole experiment. Short solute pulses of LiBr, NaBr, and $MgBr_2$ were added to the column. Experimental details for both columns are given in Nitzsche et al 1999.

Flow velocities (between 2.3 and 2.6 cm/h for different experiments) were estimated from the bromide BTCs using a 1-D CDE. The estimated flow velocity of the bromide BTCs was always about 5% smaller than the applied flux. This indicates that bromide may have been sorbed weakly to the sediment. In further analysis of the BTCs, the bromide velocities were considered identical to the water velocity. Dispersion (0.8-1.2 cm^2/h) and porosity values (0.31-0.35) for the reactive modeling was also estimated from bromide experiments.

Two different chemical interaction models were fitted. The first model describes the ion exchange as an equilibrium process given by equations (4) and (5). The second model assumes that ion exchange follows a kinetic reaction (equation 6). For both models, the equilibrium concentrations were calculated using the PHREEQC code. The equilibrium constants of Li^+, Na^+, and Mg^{2+} were estimated from the BTCs. The CEC was fitted only for the lithium data. For sodium and magnesium data, the CEC was set to the result from the lithium fit. In the case of kinetic interaction, CEC and the forward and backward reaction rates (k_f, $[h^{-1}]$, k_b $[h^{-1}]$) of Li^+, Na^+ and Mg^{2+} were estimated.

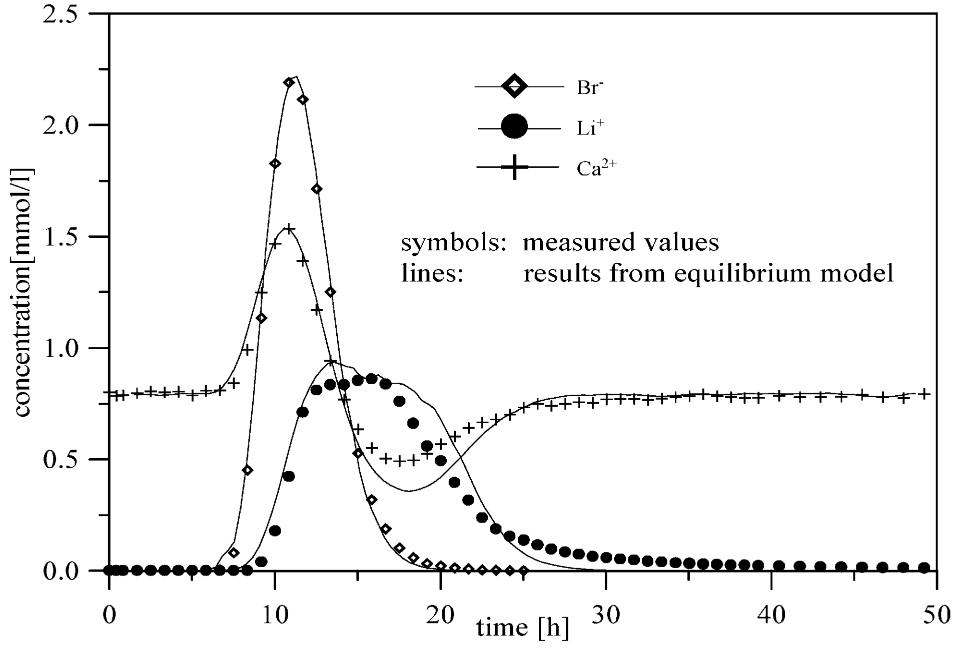

Figure 1. Fitted breakthrough curves from column experiments, using an equilibrium approach (experiment P11)

The CEC for the Na^+ and Mg^{2+} experiments was assumed equal to the value obtained for Li^+.

The equilibrium approach describes the main behavior of calcium well but the low calcium concentrations between 15 and 25 hours in the tail are clearly underestimated (see Figure 1, experiment P11). The dip in the calcium concentration below initial values corresponds with the delay in the lithium concentration in comparison with bromide. The total charge balance ($c_{Li}+2c_{Ca}-c_{Br}$) is zero within an error of less than 2.5%. The same behavior is observed for the cations in the other experiments. In the kinetic approach, different 1st order constants were used for forward and backward reactions. The kinetic constants are lumped parameters for the underlying diffusion process and may be dependent on the size and charge of ions. Equilibrium constants are relative values and are normalized to a value of 0.0 for the NaX complex.

The kinetic model describes the BTCs of lithium and calcium better then the equilibrium model (shown for experiment P12 in Figure 2). The forward rate constant of Li^+, Na^+, and Mg^{2+} is larger than the backward rate constant of Ca^{2+} (Table 1). However, the Li^+ value from experiment P12 is significantly smaller than that from experiment P11. All the backward constants are of the same order of magnitude. This may be due to the fact that this value is strongly influenced by the diffusion of Ca^{2+} ions. Forward kinetic constants of sodium and magnesium are larger (faster reaction) than the forward kinetic constant of lithium. It can be seen that the kinetic constants depend on the kind of ion that exchanges. Different ion sizes might explain such different diffusion behavior. However, the backward rates are much smaller than the forward rate for all ions. This cannot simply be explained by the different size of the calcium ions. The sorption and desorption processes are very different considering concentration of exchanging ions. In the forward reaction, a pulse of ions has to come to equilibrium with a very low concentration on the exchange places. This process is far from equilibrium when it starts. The backward reaction is very close to equilibrium (high concentration of calcium in solution and on the exchanger). If the reaction rate depends on the distance to the equilibrium (a nonlinear process, which can be observed in many kinetic reactions), the behavior observed in the experiments can be understood. However, the reaction rates are lumped parameters. A qualitative discussion of their values seems to be possible. A quantitative analysis requires the data to be fitted.

The equilibrium constants are comparable to those from the literature (Apello 1994; Appelo et al. 1997; Parkhurst and Appelo 1999). The CEC values are in the same range as those measured directly (mean 0.44 meql/100g, Englert et al. 2000).

To verify the kinetic approach, two additional experiments were done with an increased flow rate. Again, flow velocities and dispersion coefficients were taken from bromide results. The reactive parameters were taken from experiment P12 with no additional fit. Figure 3 shows the Li^+ results for 3 different velocities. The good agreement between measured concentrations and the model shows that the model is able to describe the reactive process on the column scale.

2-D modeling of tracer experiments at the test site

A large-scale tracer test with LiCl was conducted at the Krauthausen test site. Details concerning the field site and experimental layout of the wells were given by Vereecken et al. 2000. The temporal and spatial evolution of the Li^+ solute plume was monitored for 450 days by collecting groundwater samples using multi-level samplers. The groundwater samples were analyzed for Li^+ using ICP-MS. Ca^{2+}, Mg^{2+}, K^+, and Na^+ concentrations were determined on the remaining sampling volumes. Measurements showed that 90% of the molar cation concentration was found as Ca^{2+} and Li^+. For simplification, Ca^{2+} and Li^+ were further considered in the model. Anions considered were Cl^-, SO_4^{2-}, NO_3^-, and HCO_3^-. However, anion exchange processes were not taken into account. Speciation calculations using PHREEQC show that the majority of calcium ions were in the Ca^{+2} state, with only a small amount as $CaSO_4$ complexes. Lithium complexation was not found at all. Due to these facts,

Table 1. Parameter results for a Krauthausen field side sediment (from Nitzsche et al. 1999)

column	P11		P12		
CEC [mmol/L]	29		34		
CEC [mequ/100g]	0.43		0.50		
experiment	P11-1	P11-2	P12-1	P12-2	P12-3
ion	Li^+	Li^+	Li^+	Na^+	Mg^{2+}
$\log(K_{equ})^*$	-0.19	-0.19	-0.19	0.0	0.78
$k_f\,[h^{-1}]$	5.4	6.3	2.0	8.0	8.6
$k_b\,[h^{-1}]$	0.9	0.8	1.2	1.5	1.0
Recovery [%]	95.4	95.0	94.5	100.3	-

* $\log(K_{equ})$ values are normalized to a value of 0.0 for the NaX complex, the resulting CaX_2 value is 0.79

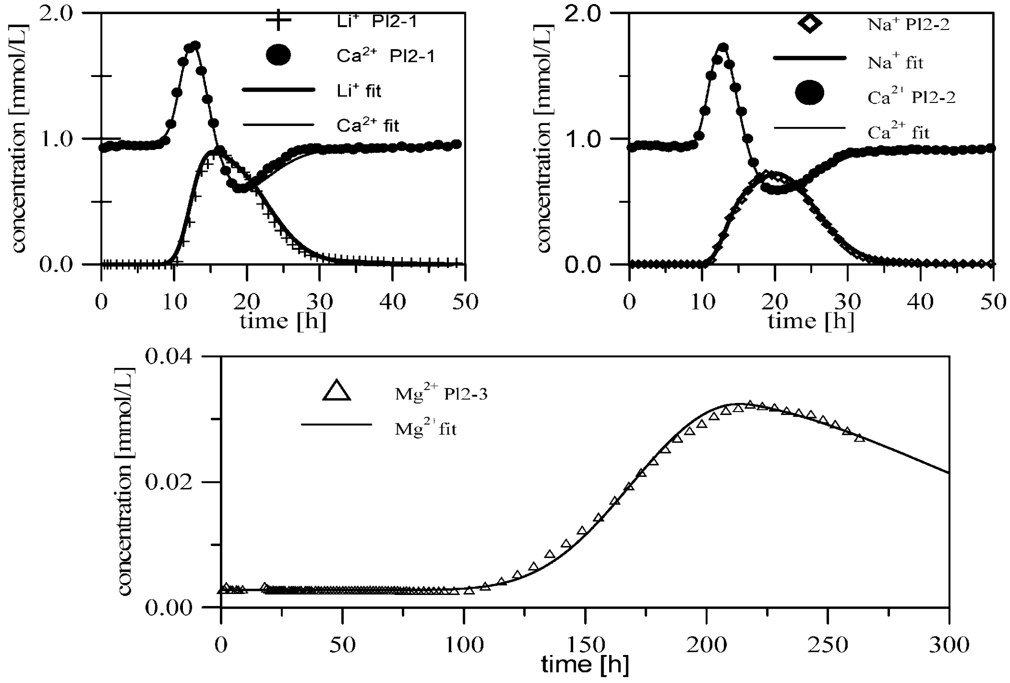

Figure 2. Fitted breakthrough curves from column experiments, using a kinetic approach (experiment P12)

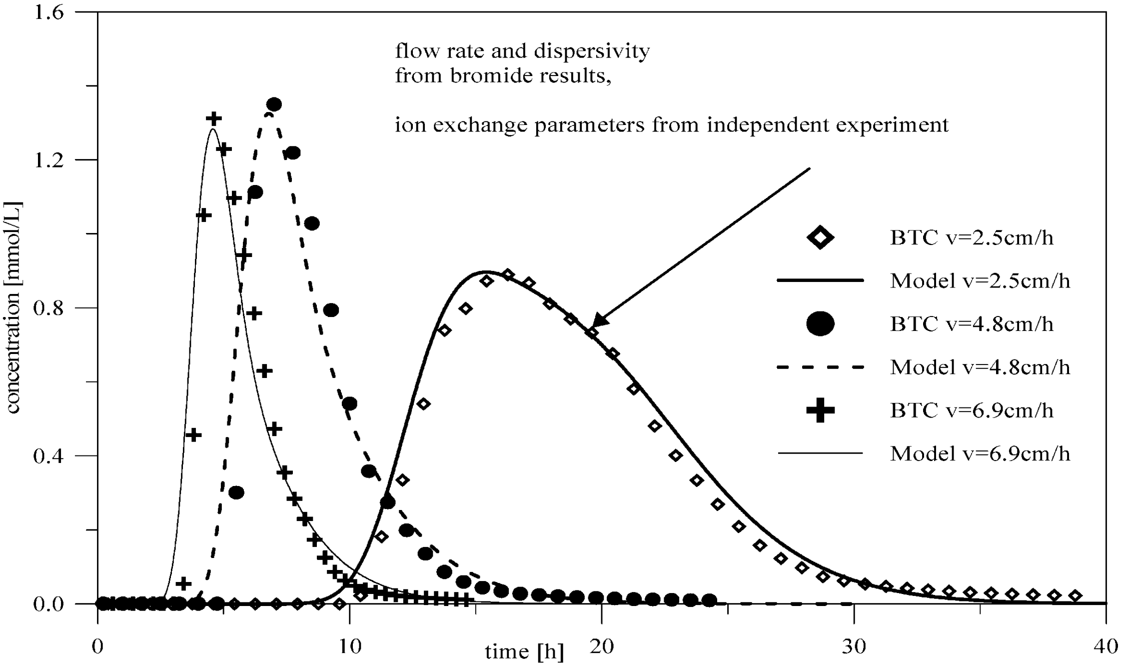

Figure 3. Breakthrough curve for lithium for three different flow rates

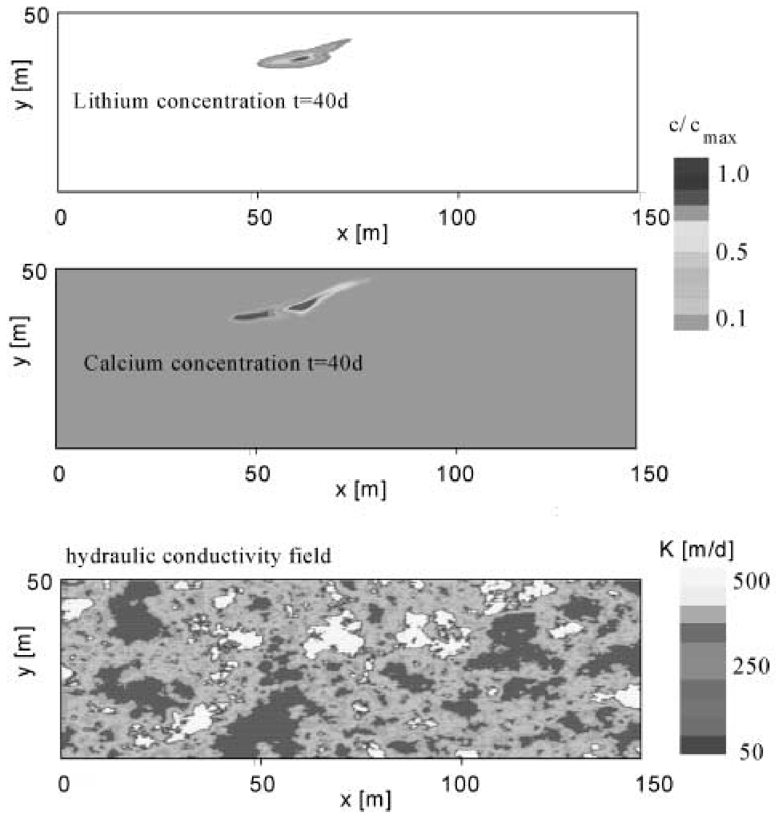

Figure 4. Hydraulic conductivity field and tracer plumes for a 2-D model

the total anion concentration was modeled as Cl^-. Measured redox potential was approximately 300mV for all wells. Iron concentrations were very low. Sulfate and nitrate reduction was not observed. The measured pH was 6.7 ± 0.1.

Solute transport of Li^+ in a 2-D porous medium in equilibrium with a $CaCl_2$ solution (3 mmol/L) was calculated using the parallel particle tracking code PARTRACE (Neuendorf 1997). The reaction steps were calculated by coupling PHREEQC to PARTRACE (Nitzsche et al. 2001). The flow domain for both simulations was 150 m by 50 m with a spatial discretization of 1 by 1 m. The time discretization was set to 0.25 d. The velocity field was calculated with the TRACE computer code, assuming a heterogeneous hydraulic conductivity field (Figure 4) with a mean value of 120 m/d and a variance of ln(K) of 1.0 using a mean gradient of 0.002. The correlation length used were 6.7m for both horizontal directions, assuming an exponential semivariogram model. These statistics were obtained from measurements at the field site (Englert et al. 2000). A nugget was not used in the model since experimental data did not indicate that doing so would be appropriate. The realization of the stochastic field was calculated with a Kraichnan generator (Schwarze 1999) within the TRACE code. It should be noted that the vertical correlation length was one order of magnitude smaller (0.6m-0.7m), but of course this could not be incorporated in a 2-D model. Li^+ was injected as a Dirac pulse with a total mass of 2830 mol. Chemical interaction was modeled using the parameters estimated from the soil column experiments. Figure 4 shows the tracer plums for both cations at 40 days after injection. Because the K field was generated stochastically, the plume position cannot be compared to field experiments. BTCs were calculated by the model at 20 m and 30 m from the injection point in the center of mass flow (Figure 5). Computing times for the model runs (400 time steps in total) were approximately 2 h on 32 CPU nodes of a CRAY-T3E machine.

In Figure 5, BTCs of lithium and calcium are shown for two observation wells located along the main flow direction of the lithium solute plume. The field BTCs of calcium show a similar behavior as was observed

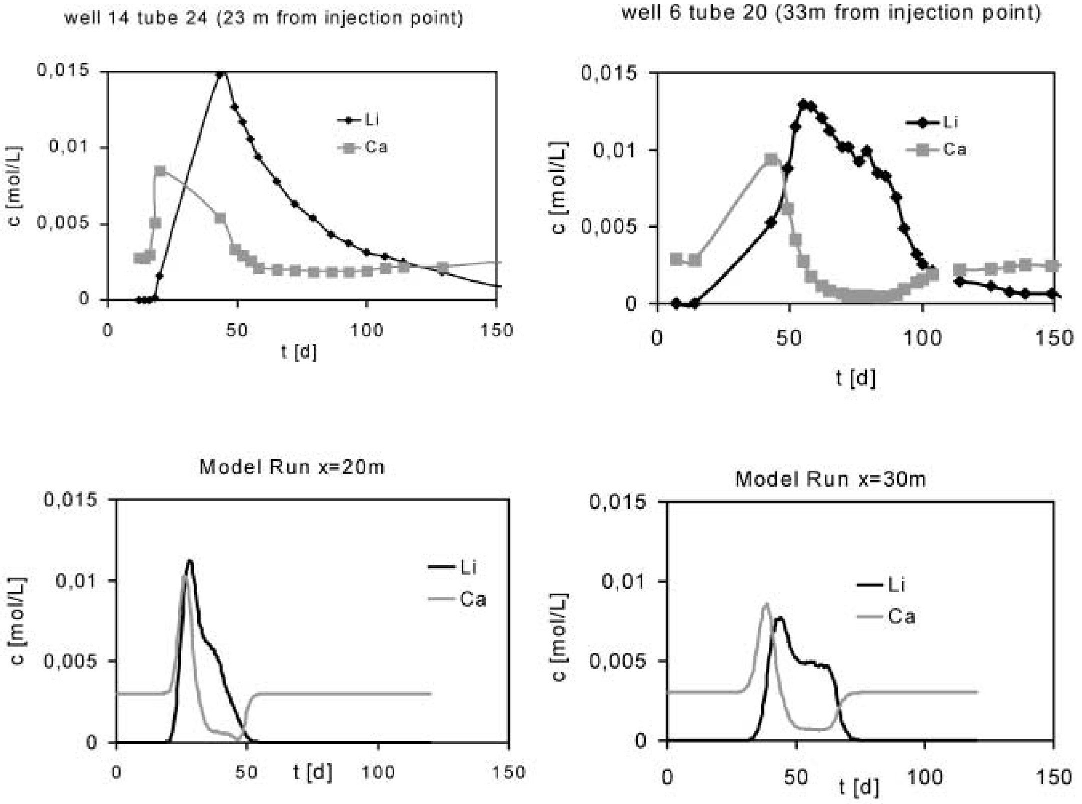

Figure 5. Breakthrough curves from field tracer experiments and results from the 2-D model

in the columns, including the dip in calcium concentrations. The error in the measured charge balance here is 5% (including all major ions). BTCs are close to one another in time. With increasing distance, the lithium BTC peak approaches the location of the minimum in the calcium concentrations. The dilution of calcium increases with distance from the injection wells.

The calculated BTCs using the 2-D CDE with kinetic interaction (without any parameter fit) show a similar behavior as the measured BTCs. However, the maximum concentration is underestimated in the model. This is due to the fact that we use a 2-D approach by averaging over the vertical dimension of the aquifer. 3-D resolved sampling from the field showed that the flow was restricted to the deeper aquifer. In fact, depth-averaged measured concentrations were smaller than predicted by the model. Macro-dispersivity and flow velocities were in the same range in both the model and the experimental results, though no fitting of velocity and dispersivity was done. Both parameters come from statistical analysis of sediment properties. However, for later times with larger plume displacements (not shown), this is no longer true. It seems that a constant set of statistical parameters in 2-D cannot describe the whole test site. Large differences between model and experimental results are shown in the tailing of the BTCs. This may be due to the presence of a physical non-equilibrium. However, kinetic parameters from column experiments no longer seem to be valid on the field scale.

Conclusions

A coupled CDE thermodynamic reaction model was used to describe solute transport in sediments. The 1-D transport- kinetic reaction model was able to fit results from column experiments using Li^+, Na^+, and Mg^{2+} pulse injections into sediment flushed with Ca^{2+}. A heterogeneous hydraulic conductivity field was simulated using a 2-D model. The parameter values in the model were obtained from the column experiments and from independent measurements without any adjustment. The results of the 2-D model qualitatively agreed with the measured field BTCs. Details in the BTCs show some unresolved questions. One reason for this is clearly the restrictions associated with a 2-D model. Other questions are raised by the scale behavior of the parameter, especially that of the kinetic rate constants. The use of 3-D models in combination with chemical heterogeneous parameters should give better results

Calculation time on the CRAY T3E supercomputer were in an acceptable range (2h for one run). For future simulations, Monte Carlo simulations with a few numbers of realizations (about 100) will be possible. Uncertainty ranges of the modeled BTCs can then be discussed.

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