

# NUMERICAL EVALUATION OF MULTICOMPONENT CATION EXCHANGE REACTIVE TRANSPORT IN PHYSICALLY AND GEOCHEMICALLY HETEROGENEOUS POROUS MEDIA

Javier Samper and Changbing Yang

*E.T.S. Ingenieros de Caminos, Canales y Puertos, Universidad de A Coruña, Spain, e-mail:  
jsamper@udc.es*

## ABSTRACT

Multicomponent cation exchange reactive transport in physically and geochemically heterogeneous porous media is evaluated by combining Montecarlo techniques and multicomponent reactive transport models for a set of three cations ( $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{+2}$ ) which undergo exchange reactions through a 2-D vertical transect. Both permeability and cation exchange capacity (CEC) of the medium are random Gaussian functions with spherical semivariograms. Spatial moments of depth-averaged concentrations of  $\text{Na}^+$ ,  $\text{Ca}^{+2}$  and  $\text{Cl}^-$  have been computed to evaluate the features of cation plumes. Numerical results indicate that the displacement of reactive plumes increases with the variance of Log K, but decreases as the variance of Log CEC increases. Second-order spatial moments increase with increasing variances of Log K and Log CEC. Cation apparent velocities depend on the variance of Log CEC and the correlation between Log K and Log CEC. Contrary to what happens in homogeneous porous media, in physically and geochemically heterogeneous porous media cation plumes do not show any coherence.

## 1. INTRODUCTION

Contaminant mixtures are usually considered to contain two or more distinct compounds that chemically interact with one another as well as with geological materials in a highly nonlinear manner. One of the most challenging aspects is the derivation of effective parameters at field scale for reactive species which migrate through heterogeneous porous formations. In comparison with the large amount of stochastic studies for a single reactive solute transport suffering adsorption [Gelhar, 1993; Miralles-Wilhelm and Gelhar, 1996; Espinoza and Valocchi, 1997; Srivastava et al., 2002; Fernández-García et al., 2004; Mojid and Vereecken, 2005; Cirpka, 2005], much less attention has been paid to multicomponent competitive cation exchange reactive transport in physically and geochemically heterogeneous aquifers. Christiansen (2000) carried out simulations of multi-species transport of cations (calcium, magnesium, potassium, sodium, and ammonium) coupled with cation exchange processes in a heterogeneous aquifer having random permeability and cation exchange capacity. He reported that chemical heterogeneities plays a minor role on effective retardation coefficient and transverse vertical dispersivity but longitudinal macrodispersivities are significantly affected by chemical heterogeneity and ion exchange. Yang and Samper (2004) and Samper and Yang (2004) presented stochastic simulations of physical and

geochemical heterogeneities for the transport of three cations ( $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{+2}$ ) in a 1-D column and evaluated the moments of concentrations. Their simulation results indicate that the impact of physical and geochemical heterogeneities on the movement of cations is significant. The larger the variance of Log K, the further the plumes extended and the larger the variance of Log CEC, the greater the cation plumes are retarded. The combined effect of simultaneous heterogeneities in Log K and Log CEC produces much longer tails and larger concentration variances. Mass transfer of cation exchange is highly nonlinear. This makes difficult to derive analytical solutions for transport equations. Samper and Yang (2006) presented an analytical method for a system of three monovalent cations ( $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$ ) based on the analytical solution of Miralles-Whilhelm and Gelhar (1996) and analyzed the effect of heterogeneities on the transport parameters of each cation. They reported that cation macrodispersivities depend on the correlation length and variance of Log K and Log CEC and their correlation structures. However, this analytical method is based on the simplification that the total weighted sum of dissolved cation concentrations is constant (the weights being equal to cation selectivities).

In this paper, we present a methodology to analyze longitudinal features of a set of chemical species which undergone cation exchange reactions in a 2-D porous medium having random Log K and Log CEC. Section 2 presents the Monte-Carlo method used for modelling the spatial distributions of permeability and CEC in an aquifer. 5 groups of numerical experiments are designed in terms of randomness of Log K and Log CEC and their correlation structures. Spatial moments and apparent velocities of two cations ( $\text{Na}^+$  and  $\text{Ca}^{+2}$ ) and a nonreactive species ( $\text{Cl}^-$ ) are calculated for the 5 groups of numerical experiments.

## 2. MONTE CARLO SIMULATION

### 2.1 Case description

Numerical simulations are performed for plumes moving through a vertical heterogeneous porous medium in the x-z plane with a size of 40 m  $\times$  10 m (Figure 1). Heads are prescribed on the left and right boundaries, yielding a uniform mean horizontal field with a mean longitudinal hydraulic gradient of  $J = -0.1$ . Top and bottom boundaries of the domain are impervious. Porosity ( $\phi$ ) is uniform and equal to 0.3.

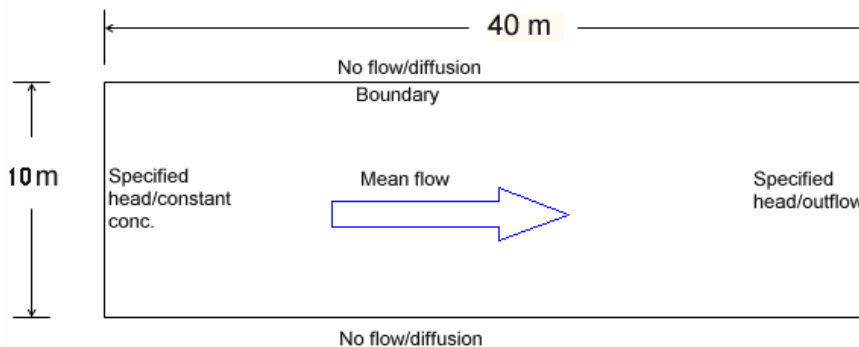
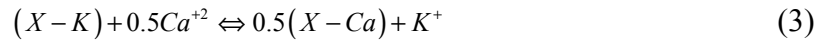
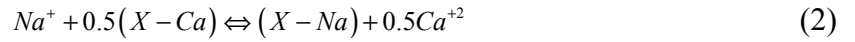


FIGURE 1. Configuration of the domain

Initially the system is filled with a water having 1 mM  $\text{NaNO}_3$  and 0.2 mM  $\text{KNO}_3$ . It is flushed by a 0.6 mM  $\text{CaCl}_2$  solution from the left boundary.  $\text{Na}^+$  is weakly adsorbed, and is

eluted first.  $K^+$  is more tenaciously held than  $Na^+$ , and it appears retarded. Nitrate is used as anion.  $Cl^-$  is used as a conservative solute to display pure transport in the heterogeneous porous medium. This case corresponds to a laboratory experiment documented in PHREEQM user's manual. Instead of the 1-D column having uniformly distributed permeability and CEC considered in that laboratory experiment, here both Log K and Log CEC are random throughout a 2-D domain.

According to the Gaines-Thomas convention, cation exchange reactions can be written as [Appelo and Postma 1993],



where (X-Na), (X-K) and (X-Ca) denote exchanged cations. Equation (3) can be obtained by adding the first two equations. Application of mass action law to reactions (1) and (2) leads to:

$$\frac{\beta_{Na} C_K}{\beta_K C_{Na}} = k_1 \quad (4)$$

$$\frac{\beta_{Na} C_{Ca}^{0.5}}{\beta_{Ca}^{0.5} C_{Na}} = k_2 \quad (5)$$

where  $k_1$  and  $k_2$  are selectivity coefficients of  $Na^+$  to  $K^+$  and  $Na^+$  to  $Ca^{+2}$ , respectively. In this study,  $k_1$  and  $k_2$  are equal to 0.2 and 0.4, respectively.  $\beta_{Na}$ ,  $\beta_K$  and  $\beta_{Ca}$  are equivalent fractions of exchanged cations  $Na^+$ ,  $K^+$  and  $Ca^{+2}$ , respectively, which add to one:

$$\beta_{Na} + \beta_K + \beta_{Ca} = 1 \quad (6)$$

Transport equations for cations suffering cation exchange reactions is given by,

$$\frac{\partial C_i}{\partial t} + \frac{\partial W_i}{\partial t} = \nabla \cdot (\mathbf{D} \nabla C_i) - \mathbf{v} \nabla C_i \quad (7)$$

where  $C_i$  is the concentrations of the  $i^{\text{th}}$  dissolved cation ( $i=Na^+$ ,  $Ca^{+2}$  and  $K^+$ ) (mol/l);  $W_i$  is the concentrations of exchanged cations (mol/l);  $\mathbf{D}$  is the local dispersion coefficient ( $L^2/T$ ) and  $\mathbf{v}$  is the velocity of water ( $L/T$ ) which is computed from Darcy's law.

Concentrations of exchanged cations  $W_i$  in (7) are related to equivalent fractions through

$$W_i = \frac{\beta_i}{z_i} \frac{CEC \rho_d}{100\phi} \quad (8)$$

where CEC is cation exchange capacity (meq/100g of solid),  $\phi$  is porosity (-),  $z_i$  is cation charge,  $\rho_d$  is dry density ( $g/cm^3$ ) and  $i = Na^+$ ,  $K^+$  and  $Ca^{+2}$ .

In all simulations, local longitudinal and transverse dispersivities are equal to 0.2 m and 0.15 m, respectively. Molecular diffusion is neglected. Parameter values used in the calculations are listed in Table 1.

## 2.2 Simulation of Log K and Log CEC fields

It is well documented that permeability shows spatial variability due to the natural heterogeneity of porous media. The spatial variability of Log K can be characterized by semi-variograms [Gelhar, 1993]. Several researchers have reported that CEC of soils also shows

variations in space and can be regarded as a stochastic field with a spatial correlation structure [Cassel et al., 2000]. Jacques et al. (1999) reported that the experimental vertical semivariograms of the residuals of 93 samples of CEC showed a spatial correlation structure. The correlation length ranges from 0.25 to 0.40 m. Christiansen (2000) also reported a negative correlation between Log CEC and Log K of -0.85 for a calcareous aquifer layer and -0.69 for a non-calcareous aquifer layer from 256 field data.

TABLE 1. Parameters used in the calculations.

Parameters	Values
Domain size (m <sup>2</sup> )	40x10
Porosity	0.3
Local longitudinal dispersivity (m)	0.2
Local transverse dispersivity (m)	0.15
Hydraulic gradient	-0.1
Number of elements	20000
Number of nodes	10251

In this study, Log K and Log CEC are assumed to be a random Gaussian functions with isotropic spherical semivariograms. Realizations of Log K and Log CEC are derived with the Monte Carlo simulator, GCOSIM3D [Gómez-Hernández, 1993]. Simulations of Log K and Log CEC are performed on 100 by 50 quadrilateral elements. Afterwards, simulated values of permeability and CEC in each element are assigned to the two triangular finite elements and are taken as input parameters for reactive transport modelling.

5 groups of numerical experiments are designed in terms of Log K and Log CEC and their correlation structures. Means of Log K and Log CEC are taken equal to 1.1 and -3.85, respectively. Their correlation lengths are equal to 0.4 m, that is, two times the element size. Group A is designed to investigate the effect of increasing variability of permeability on the movement of solute plumes while CEC is assumed to be uniformly distributed in the aquifer. Group B aims at evaluating the effect of increasing the variability of Log CEC on reactive solute transport while permeability is assumed uniform. The effect of their correlation is analyzed in groups C (uncorrelated), D (positive correlation) and E (negative correlation). Although in general Log K and Log CEC are not perfectly correlated [Jacques et al., 1999], in this study they are assumed to be perfectly correlated in groups D and E according to:

$$\text{LogCEC} = a\text{LogK} + b \quad (9)$$

where  $a$  and  $b$  are parameters. Parameter  $a$  is greater than 0 for a positive correlation and less than 0 for a negative correlation. A negative correlation between Log K and Log CEC indicates that a zone with a low permeability has a large cation exchange capacity and viceversa a zone with a high permeability has a small cation exchange capacity.

For illustration purposes Figure 2 shows the spatial distributions a realization of Log K and Log CEC in which their means and variances are equal to 1.099 and 0.5 for Log K and -3.85 and 1.0 for Log CEC, respectively. Log K and Log CEC are negatively correlated. One can see that zones with large permeabilities have low values of CEC and viceversa.

CORE<sup>2D</sup> is used to solve flow and reactive transport coupled with cation exchange reactions. CORE<sup>2D</sup> is an extended and improved version of TRANQUI (Xu et al., 1999) that has undergone extensive verification and has been used to model laboratory tests and field case studies [Samper et al., 2003, Dai and Samper, 2004]. It is worth noting that reactive transport calculations for a single realization take 10 hours on a PC having a CPU of 3.2 GHz.

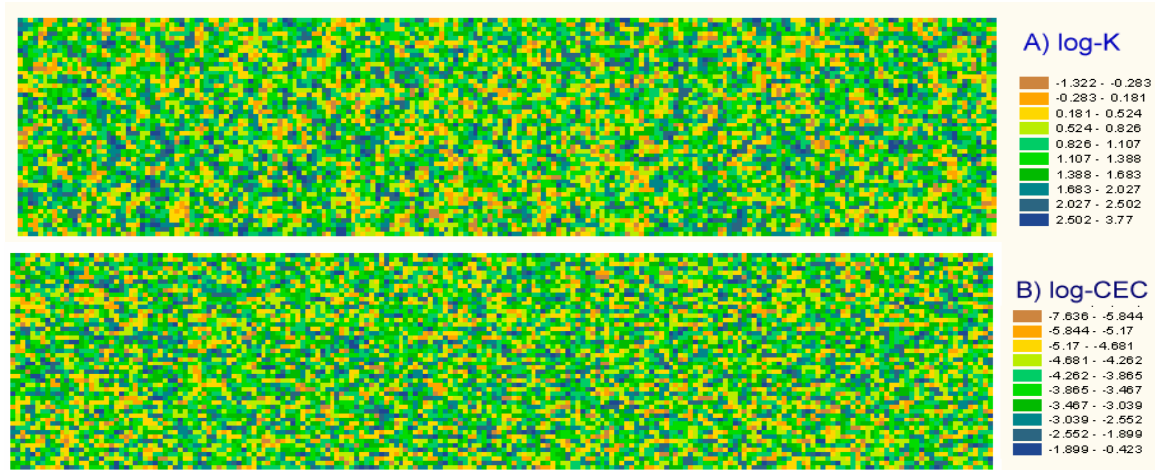


FIGURE 2. Spatial distributions of a selected realization of Log K (A) and Log CEC (B).

### 3. SPATIAL MOMENTS

If permeability is random, groundwater velocity is also random. Once are released into the system, solutes move with groundwater along random flow paths and simultaneously exchange with interlayer cations. First- and second-order spatial moments for a continuous injection source can be calculated by

$$X_i(t) = \frac{m_{i,1}(t)}{m_{i,0}(t)} \quad (10)$$

$$\sigma_{i,2sc}^2 = \frac{m_{i,2}(t)}{m_{i,0}(t)} - \left(\frac{m_{i,1}(t)}{m_{i,0}(t)}\right)^2 \quad (11)$$

where  $m_{i,0}$ ,  $m_{i,1}$  and  $m_{i,2}$  are calculated by [Jose et al., 2004]:

$$m_{i,0}(t) = \int_{-\infty}^{\infty} q_i(x,t) dx \quad (12)$$

$$m_{i,1}(t) = \int_{-\infty}^{\infty} xq_i(x,t) dx \quad (13)$$

$$m_{i,2}(t) = \int_{-\infty}^{\infty} x^2q_i(x,t) dx \quad (14)$$

Where  $q_i(x,t)$  is the spatial derivative of solute concentration. Apparent velocities of cations can be obtained from Equation (10) through

$$v_a = \frac{\partial X_i(t)}{\partial t} \quad (15)$$

First-order spatial moments depend on the variances of Log K and Log CEC and their correlation structures. The greater the variance of Log K, the larger the displacements of the plume fronts for both nonreactive and reactive species. This conclusion is consistent with those of Gelhar (1993) and Espinoza and Valocchi (1997) for a single species. The effect of variance of Log CEC on the displacement of reactive plumes is significant. The larger the variance of Log CEC, the smaller the displacement of the plume front. Displacement of the reactive plume front depends on the correlation structure between Log CEC and Log K. A negative correlation structure leads to a larger displacement of the reactive plume than in the case of uncorrelated and positive correlation because for the case of negative correlation cations migrate easily through high permeability zones where cation exchange is mild (due to a small cation exchange capacity). It is worth noting that the displacement of the plumes of

$\text{Na}^+$ ,  $\text{Ca}^{+2}$  and  $\text{Cl}^-$  are different in all simulations. In the case of only Log K to be random, the displacement of  $\text{Cl}^-$  is almost 5 times of that of  $\text{Na}^+$  and 7.5 times of that of  $\text{Ca}^{+2}$ .

Second-order spatial moments of cations, which measure the extent of cation plumes, depend on the variances of Log K and Log CEC and their correlation structures. Figure 3A shows the plots of second-order spatial moments of  $\text{Na}^+$  and  $\text{Ca}^{+2}$  for different variances of Log K. One can see that second-order spatial moments of the plume fronts of two reactive species increase with time. The larger the variance of Log K, the larger the second-order spatial moments of  $\text{Na}^+$  and  $\text{Ca}^{+2}$ . Figure 3B shows the second-order spatial moments of  $\text{Na}^+$  and  $\text{Ca}^{+2}$  as a function of time for different variances of Log CEC. Second-order spatial moments of  $\text{Na}^+$  and  $\text{Ca}^{+2}$  increase with variance of Log CEC. Second-order spatial moments of  $\text{Na}^+$  and  $\text{Ca}^{+2}$  are greater for an uncorrelated structure than those for a positive correlation, while less than those for a negative correlation. It can also be seen that the second-order spatial moments of  $\text{Na}^+$  are different than those of  $\text{Ca}^{+2}$ . Second-order spatial moment of  $\text{Na}^+$  is almost 2 times of that of  $\text{Ca}^{+2}$  in the case of variance of Log K to be 0.1 and the difference of second-order spatial moments increases with variance of Log K (see Figure 3A).

Figure 4A shows comparison of apparent velocities of  $\text{Na}^+$  and  $\text{Ca}^{+2}$  for different variances of Log K. It can be seen that apparent velocities of  $\text{Na}^+$  and  $\text{Ca}^{+2}$  increase with time and asymptotically approach constant values. Apparent velocities of  $\text{Na}^+$  and  $\text{Ca}^{+2}$  slightly increase with increasing variance of Log K. Asymptotic values of apparent velocities of  $\text{Na}^+$  and  $\text{Ca}^{+2}$  are 0.062 m/day and 0.093 m/day, respectively. Apparent velocities of the reactive plume decrease with increasing variance of Log CEC. The larger the variance of Log CEC, the smaller the apparent velocities (not shown here). Figure 4B shows the comparison of apparent velocities of plume fronts for  $\text{Na}^+$  and  $\text{Ca}^{+2}$  for different correlation structures between Log K and Log CEC. One can see that the apparent velocities of  $\text{Na}^+$  is greater than that of  $\text{Ca}^{+2}$ . Apparent velocities increase slightly with time from 0.03 to 0.04 m/day for  $\text{Ca}^{+2}$  and from 0.05 to 0.07 m/day for  $\text{Na}^+$ . There is no significant difference in apparent velocities for different correlation structures. It is worth noting that movements of the plume fronts of cations involved in cation exchange reactions are coherent with those occurring in a homogeneous aquifer. This also is a basic assumption for analytical solutions for multication exchange reactive transport developed by Charbeneau (1988). However, in physically and geochemically heterogeneous porous media, macroscale cation plume fronts do not show any coherence.

Both permeability and cation exchange capacity (CEC) of the medium are random Gaussian functions with spherical semivariograms. Spatial moments of depth-averaged concentrations of  $\text{Na}^+$ ,  $\text{Ca}^{+2}$  and  $\text{Cl}^-$  are have been computed to evaluate the features of cation plumes. Numerical results indicate that the displacement of reactive plumes increases with the variance of Log K, but decreases as the variance of Log CEC increases. Second-order spatial moments increase with increasing variances of Log K and Log CEC. Cation apparent velocities depend on the variance of Log CEC and the correlation between Log K and Log CEC. Contrary to what happens in homogeneous porous media, in physically and geochemically heterogeneous porous media cation plumes do not show any coherence.

#### 4. CONCLUSIONS

Multicomponent cation exchange reactive transport in physically and geochemically heterogeneous porous media has been evaluated with Montecarlo simulation and reactive

transport modeling for a set of three cations ( $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{+2}$ ) which undergo exchange reactions through a 2-D vertical transect. Spatial moments and apparent velocities of reactive and conservative species were computed for a wide range of variances of Log K and Log CEC and different assumptions regarding their cross-correlation. Numerical results indicate that the greater the variance of Log K, the larger the displacement and apparent velocity of a plume front, but the larger the variance of Log CEC, the smaller the displacement and apparent velocity of a reactive plume front. Apparent velocities depend on the correlation structure. Cation plume fronts do not show any coherence at macro scale in a physically and geochemically heterogeneous porous medium while this is true in a homogeneous porous medium. The displacement of  $\text{Na}^+$  is greater than that of  $\text{Ca}^{+2}$ . Second-order spatial moments of the plume fronts of the two reactive species increase with time. The larger the variances of Log K and Log CEC, the greater the second- order spatial moments. Second-order spatial moments of  $\text{Na}^+$  and  $\text{Ca}^{+2}$  are greater for an uncorrelated structure than those for a positive correlation structure while less than those for a negative correlation structure.

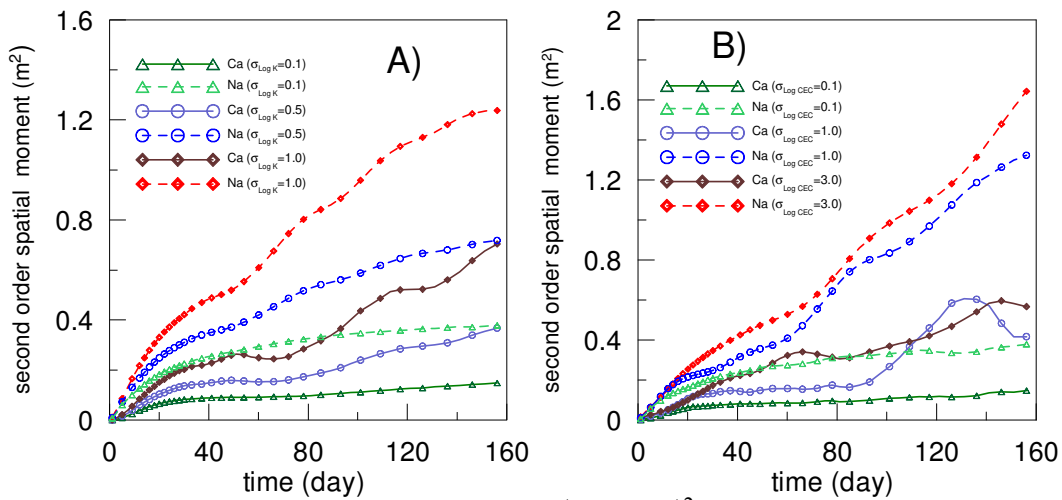


FIGURE 3 Second-order spatial moments of  $\text{Na}^+$  and  $\text{Ca}^{+2}$  for A) only Log K is random, B) only Log CEC is random

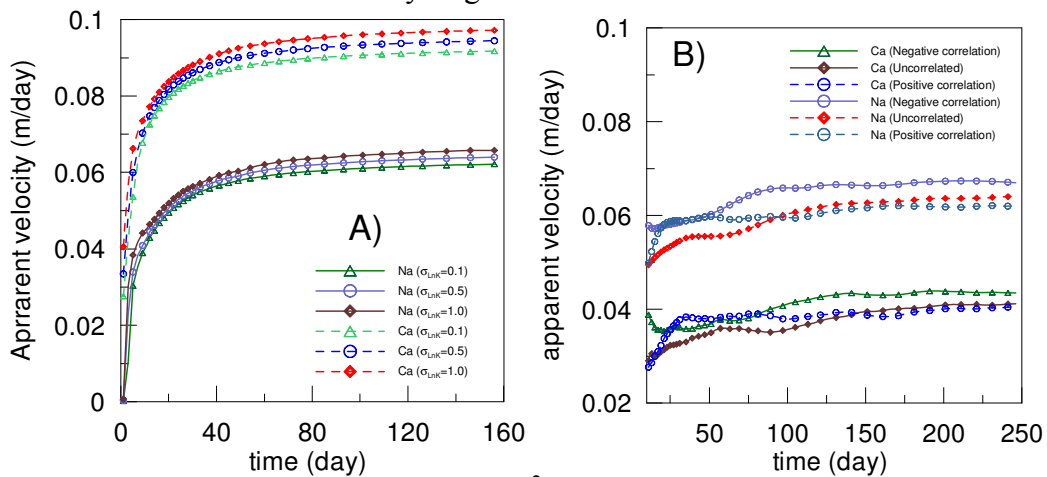


Figure 4 Apparent velocities of  $\text{Na}^+$  and  $\text{Ca}^{+2}$  for different variances of Log K (left) and correlation structures between Log K and Log CEC for variances of Log K and Log CEC equal to 0.5 and 1, respectively (right).

## REFERENCES

- Appelo, C.A.J., and D. Postma (1994), *Geochemistry, groundwater and pollution*, Balkema, Rotterdam, Netherlands.
- Cassel, D.K., O. Wendroth, and D. R. Nielsen (2000), Assessing spatial variability in an agricultural experiment station field: opportunities arising from spatial dependence, *Agron J.*, 95, 706-714.
- Charbeneau, R. J. (1988), Multicomponent exchange and subsurface solute transport: characteristics, coherence and the Reimann problem, *Water Resour. Res.*, 24, 57-64.
- Cirpka O. A. (2005), Effects of sorption on transverse mixing in transient flows, *J. Cont. Hydrol.*, 78(3): 207-229.
- Dai, Z., and J. Samper (2004), Inverse problem of multicomponent reactive chemical transport in porous media: Formulation and applications, *Water Resour. Res.*, 40, w07407, DOI 10.1029/2004WR003248.
- Espinoza, C., and A. J. Valocchi (1997), Stochastic analysis of one dimensional transport of kinetically absorbing solutes in chemically heterogeneous aquifers, *Water Resour. Res.*, 33(4), 2081-2088.
- Fernández-García, D., T.H. Illangasekare, H. Rajaram (2004), Conservative and sorptive forced-gradient and uniform flow tracer tests in a three-dimensional laboratory test aquifer, *Water Resour. Res.*, 40, W10103.
- Gelhar, L.W. (1993), *Stochastic subsurface hydrology*, Prentice-Hall, New Jersey.
- Gómez-Hernández, J.J. (1993), Programas complementarios para el análisis estocástico del transporte de radionucleidos, Technical report, ENRESA, Madrid (in Spanish).
- Jacques, D., C. Mouvet, B. Mohanty, H. Vereecken, and J. Feyen (1999), Spatial variability of atrazine sorption parameters and other soil properties in a podzoluvisol, *J. Cont. Hydrol.*, 36: 31-52.
- Jose, S.C., M.A. Rahman, and O.A. Cirpka (2004) Large-scale sandbox experiment on longitudinal effective dispersión in heterogeneous porous media. *Water Resour Res* 40: W12415 DOI 10.1029/2004wr003363.
- Miralles-Wilhelm, and F., L.W. Gelhar (1996), Stochastic analysis of sorption macrokinetics in heterogeneous aquifers, *Water Resour. Res.*, 32(6), 1541-1549.
- Mojid, M.A., and H. Vereecken (2005), On the physical meaning of retardation factor and velocity of a nonlinearly sorbing solute, *J. Hydrol.*, 302, 127-136.
- Samper, J., C. Yang, and L. Montenegro (2003), Users Manual of CORE<sup>2D</sup> Version 4: a COde for groundwater flow and REactive solute transport, Technical report, Universidad da Coruña, La Coruña, Spain.
- Samper, J., and C. Yang (2004), Transporte reactivo multicomponente en medios porosos con heterogeneidades hidrodinámicas y geoquímicas, VIII Simposio de Hidrogeología Zaragoza, Spain, pp 575-584 (in Spanish).
- Samper, J., and C. Yang (2006), Stochastic analysis of transport and multicomponent competitive monovalent cation exchange in aquifers, *Geosphere*, in press.
- Srivastava, R., P.K. Sharma, and M.L. Brusseau (2002), Spatial moments for reactive transport in heterogeneous porous media, *J. Hydrol. Engi.*, 7(4), 336-341.
- Yang, C., and J. Samper (2004), Multicomponent reactive transport in hydrodynamically and geochemically heterogeneous porous media: Eos (Transactions, American Geophysical Union) 85(47) Fall meeting supplement, abs. H33F-0541.
- Xu, T., J. Samper, C. Ayora, M. Manzano, and E. Custodio (1999), Modeling of non-isothermal multicomponent reactive transport in field scale porous media flow system, *J. Hydrol.*, 214, 144-164.