Concurrent transport of reactive and non-reactive ions in undisturbed soil columns

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A b s t r a c t. Advective-dispersive contaminant transport in soils continues to be a subject of extensive studies. Transport of conservative tracers, *ie* non-reactive ions, is mostly affected by soil physical heterogeneity that causes differences in mobility of different parts of soil solution. Transport of reactive contaminants is affected by both physical and chemical heterogeneity. The objective of this study was to observe the effects of soil structure and flow velocity on the transport of reactive calcium and sodium ions. Undisturbed southern chernozem and chestnut soil columns were used to monitor the concurrent chloride, calcium and sodium transport in slow-flow and fast-flow breakthrough experiments. Parameters of the advective-dispersive transport were estimated by fitting the advective-dispersive equation to the reduced break-through data. At low velocities, transport seemed to occur in pores having a wide range of effective diameters. Diffusion and slow transport in fine pores caused slow effluent concentration changes at the late stages of the transport. Creating fast flow resulted in a decrease in the proportion of pore space providing the initial breakthrough and in an increase in the proportion of pore space participating in the diffusion-driven mass exchange as compared with the slow-flow transport. Transport of reactive ions was affected by the flow rates in the same way as the transport of the conservative tracers. Flow rate effects on the transport were more pronounced in the chestnut soil that had poorer structure as compared with the chernozem soil.

K e y w o r d s: transport, reactive and non-reactive ions, soil

INTRODUCTION

Advective-dispersive transport of adsorbing chemicals in soils is the subject of extensive studies. Soil heterogeneity affects such transport. Transport of conservative tracers *ie* non-reactive ions, is mostly affected by soil physical heterogeneity that causes differences in mobility of different parts of soil solution. Soil solution can be provisionally divided into mobile and immobile parts (van Genuchten and Wierenga, 1976; Korsunskaya *et al.*, 1986; Pachepsky *et al.*, 2000). Because of the chemical heterogeneity of soils, different parts of soil pore surfaces have different affinities to the chemicals moving in soils. Soil pore surfaces are often conditionally divided into fast- and slow-adsorbing parts with different adsorbing capacities (Selim *et al.*, 1992; 1999). The relative importance of the two types of soil heterogeneity depends both on the soil properties and on the properties of the chemical.

Observing simultaneous transport of conservative tracers and reactive contaminants and examining differences in transport of the two types of chemicals should provide an insight into the relative role of the chemical heterogeneity in the transport of reactive chemicals. The objective of this work was to compare the transport of the chloride ion as a conservative tracer to the transport of reactive ions of calcium and sodium in undisturbed soil columns of two major agricultural soils from Southern Russia.

MATERIALS AND METHODS

Undisturbed southern chernozem and chestnut soil columns were used to monitor the concurrent chloride, calcium and sodium transport. The columns - 5 cm ID and 10 cm in height - were sampled in Stavropol region at depths from 5 to 15 cm. Selected chemical and physical properties of the soils are shown in Table 1.

The advective-dispersive transport was studied with flow rates ranging from 0.7 to 11.7 cm day^{-1}. The slow and the fast flows were created in each column by maintaining

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Ta b l e 1. Selected soil properties

Soil	Depth (cm)	Bulk density (g cm^{-3})	Percentage of particles < 1 μm	$C_{org.}$	pH in KCl	Exchangeable cations (meq 100 g^{-1})			
						Ca^{2+}	Mg^{2+}	K$^+$	Na$^+$
Southern chernozem	0-30	1.38	28.7	2.10	7.30	20.9	19.0	0.97	2.35
Chestnut soil	0-30	1.61	20.6	1.70	7.65	13.8	13.4	0.90	16.80

different heights of the influent solution above the soil surface. The slow rates varied from 0.7 to 1.3 m day^{-1}, the fast ones were in the range from 5.7 to 11.7 cm day^{-1}. At the slow rate, each column received (a) a pulse of 0.001N CaCl$_2$ solution, (b) a pulse of 0.1N CaCl$_2$ solution, (c) a pulse of 0.05N CaCl$_2$ and 0.05N NaCl solution, (d) a pulse of 0.001N CaCl$_2$. Then this sequence was repeated with the fast flow rate. Each of the pulses was terminated when concentrations of any of the three studied ions in the effluent became equal within the 1% accuracy window to the concentrations in the influent. Ion selective electrodes (Radelkis, Hungary) were used to measure ion concentrations in the effluent.

Data on the effluent concentrations were presented as breakthrough curves, *ie* dependencies of relative concentrations C$_{rel}$ on the relative effluent volume V$_{rel}$. The relative concentrations were computed as:

$$C_{rel} = \frac{C_0 - C}{C_0 - C_i}, \qquad (1)$$

where: C_i is the concentration in the influent, and C_0 is the concentration in the control experiment. The relative effluent volume was computed as $V_{rel}=V/V_{pore}$, where V_{pore} is the pore volume of the column.

The advective-dispersive equation in the form:

$$R \frac{\partial C_{rel}}{\partial V_{rel}} = \frac{D}{qL} \frac{\partial^2 C_{rel}}{\partial X^2} - \frac{\partial C_{rel}}{\partial X}, \qquad (2)$$

was used to simulate chloride transport in the soil columns. Here D is the dispersion coefficient, cm^2 day^{-1}, q is the flow rate cm day^{-1}, L is the column length, cm, R is the retardation coefficient, X is the relative distance from the top of the column, $0 \le X \le 1$ (Korsunskaia and Shein, 2001). The software CXFIT (Toride *et al.*, 1995) was used to fit the semi-infinite interval solution of the Eq. (2) to the chloride breakthrough curves to estimate the parameters. Visual inspection of the shapes of the breakthrough curves was used to find indications of the presence of preferential flow pathways and to assess the distributions of pore velocities (Pandey and Gupta, 1983; Valles *et al.*, 1990; Strock *et al.*, 2001). Such information was derived mostly from the chloride breakthrough curves. Using conservative tracers for that purposes had been proposed and justified earlier (Pfannkuch, 1963; Dankwerts, 1953; Valles *et al.*, 1990).

Preliminary tests were made to evaluate the reproducibility of breakthrough curves measured presumably under the same conditions. Some results of such tests are shown in
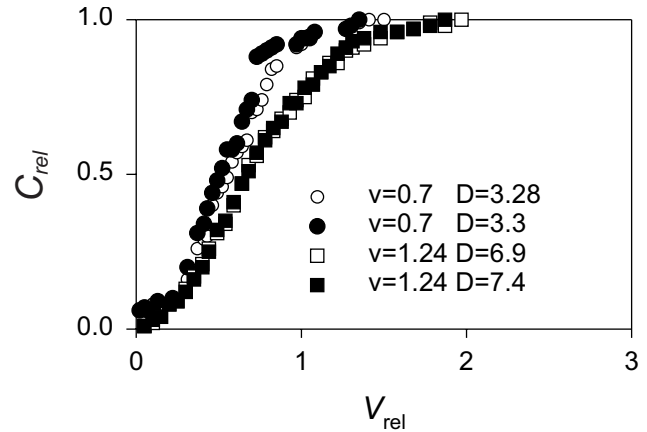

Fig. 1. Replicated chloride breakthrough curves; $\bigcirc$ and $\bullet$ first run, $\square$ and $\blacksquare$ second run, hollow and filled symbols show measurements made with two independently calibrated ion selective electrodes.

Fig. 1 for the southern chernozem. The breakthrough curves were compared for two pulses of 0.1N CaCl$_2$ separated by elution with 0.001N CaCl$_2$. Chloride contents were measured with two ion-selective electrodes for each of the two breakthroughs. The breakthrough curves appeared to be close visually; the transport parameters were also close (Table 2).

RESULTS AND DISCUSSION

Data on CaCl$_2$ transport in the studied soils are shown in Figs 2 and 3. Breakthrough curves in replications are very close for the southern chernozem at low flow rates of 0.72 to 1.4 cm day^{-1} (Fig. 2a). The transport parameters are also very close (not shown). The shapes of the breakthrough curves suggest that the transport occurs in pores having a wide range of effective diameters. The inflection of the breakthrough curves is caused mostly by dispersion in large pores. Diffusion and slow convective transport in fine pores cause slow effluent concentration changes at the late stages of the transport. Changes in the flow rates modify the shapes of the breakthrough curves from the same columns (Fig. 2b). Only one column has breakthrough curves with inflection in the range of relative concentrations from 0 to 0.5. All other columns have breakthrough curves with an interval of fast increase starting from the first portions of the effluent. Such a shape of breakthrough curves is typical for soil pore structures with preferential pathways including a relatively

T a b l e 2. Parameters of the advective-dispersive equation for data shown in figures in this paper

Figure	Symbol	q (cm day^{-1})	D (cm day^{-1})
1	○	0.70	3.28
1	●	0.70	3.30
1	□	1.24	6.90
1	■	1.24	7.41
6a	◑	0.8	32.8
6a	△	0.8	518
6a	□	0.8	142
6a	●	5.7	2526
6a	▲	5.7	2915
6a	■	5.7	509
6b	○	1.06	36.4
6b	△	1.06	17.9
6b	□	1.06	72.1
6b	●	7.3	304
6b	▲	7.3	474
6b	■	7.3	267
7a	○	0.94	29.2
7a	△	0.94	6.4
7a	□	0.94	85.3
7a	●	5.7	248
7a	▲	5.7	555
7a	■	5.7	40.5
7b	○	1.2	36.4
7b	△	1.2	17.9
7b	□	1.2	72.1
7b	●	8.1	324
7b	▲	8.1	15.8
7b	■	8.1	14.8

small part of pore space. These pathways carry chemicals through soil very fast because the pore water velocity in such preferential flow paths is relatively high. The dispersion is caused by the mass exchange between preferential pathways and the bulk of soil rather than by variations in pore water velocities within pores of large range as it has been in slow-flow experiments. Creating fast flow causes a smaller part of pore space to work for the breakthrough transport and a larger part of pore space to participate in diffusion-driven mass exchange as compared with the slow flow transport.

The chestnut soil demonstrates much more developed preferential flow as compared with the southern chernozem (Fig. 3a, b). The absence of inflection and intervals of the fast rise of relative concentrations are pronounced in all but one columns, even at the low flow rates (Fig. 3a). High flow rates exacerbate differences in the mobility of different parts of pore water (Fig. 3). The change in relative concentration from 0 to 0.7 occurs after only one pore volume is accumulated in the effluent. At the same time, the tail of the breakthrough curve is very long. This indicates that some parts of pore space, mostly fine pores, have a poor connection with the preferential flow pathways. In general, more dispersion can be seen in the chestnut soil than in the southern chernozem columns; the average value of the dispersion coefficient is 25.0±14.2 cm^2 day^{-1} as compared with values of 4.0±1.9 cm^2 day^{-1} in the chernozem. The difference in dispersion coefficients in the two soils is tenfold in fast flow experiments.

The differences in Cl breakthrough in the two soils can be, at least partly, explained by the differences in pore size distributions. Comparison of differential porosity for the two soils in this study has shown that pore size distribution in the chestnut soil reflects the presence of a large number of fine pores with the effective diameters less than 0.01-0.06 mm. The pore size distribution for the chernozem showed the presence of a much larger range of pore sizes (Korsunskaia and Shein, 2001). The chestnut soil was also more compacted as compared with the southerm chernozem
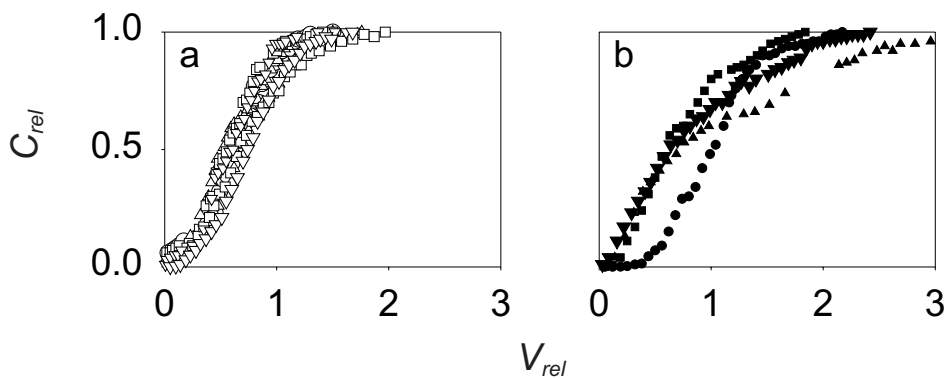

Fig. 2. Chloride breakthrough curves in southern chernozem cores from low-flow (a) and fast-flow (b) experiments. Different symbols refer to different cores.
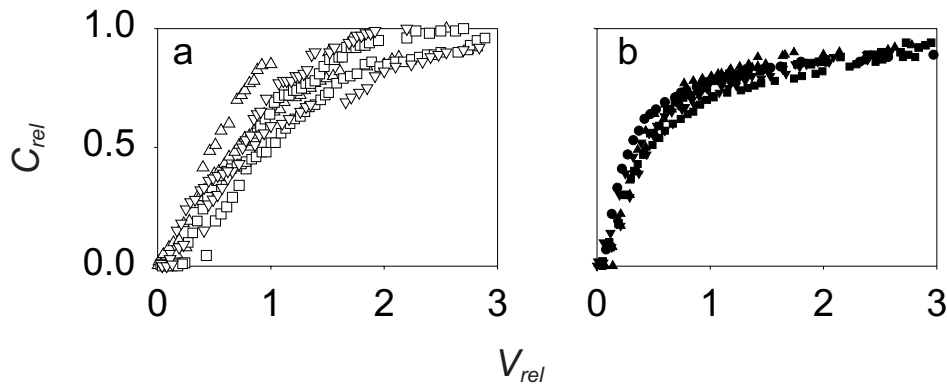
Fig. 3. Chloride breakthrough curves in chestnut soil cores from low-flow (a) and fast-flow (b) experiments. Different symbols refer to different cores.

(Table 1). Pores smaller than 0.1 mm may constitute more than 50% of pore space in such compacted soils (Domzhal *et al.*, 1990). The domination of fine pores in the chestnut soil results in the larger role of such pores in the convective dispersive transport in this soil as compared with the chernozem.

Data on $CaCl_2$ transport before and after the pulse of $CaCl_2$ +NaCl are compared in Figs 4 and 5. Note that the actual concentrations after the pulse are decreasing as the leaching progresses. However, the relative concentrations computed with Eq. (1) increase both before and after the pulse allowing the comparison. The pulse changes the Cl breakthrough in the chernozem (Fig. 4). The differences can be seen better in the slow-flow experiments. The longer tails of the after-pulse breakthrough curves imply some disaggregation and formation of additional fine pores caused by the presence of sodium ion. The fast-flow experiments show the coincidence of initial sections on

breakthrough curves before and after the pulse in three of the four columns. This can be interpreted as a 'memory' in pathways similar to the one shown in field experiments (Shein and Marchenko, 2000). A more extensive tailing is also seen in fast flow experiments after the pulse.

Comparison of before- and after-pulse Cl breakthrough curves for the chestnut soil (Fig. 5) reveals more extensive tailing after the pulse in slow-flow experiments. That can be attributed to the effect of sodium ion on soil structure similar to that in the chernozem. The fast flow experiments resulted in breakthrough curves that were similar before and after the $CaCl_2$+NaCl pulse. One possible explanation is based on the assumption that the preferential pathways occupy a small part of the pore space. The fast pulse moves predominantly through these pathways and a relatively small fraction of pore surface can be affected by the sodium solution. Another reason can be the relatively short duration of the fast-flow experiments, so that the cation exchange kinetics was slow
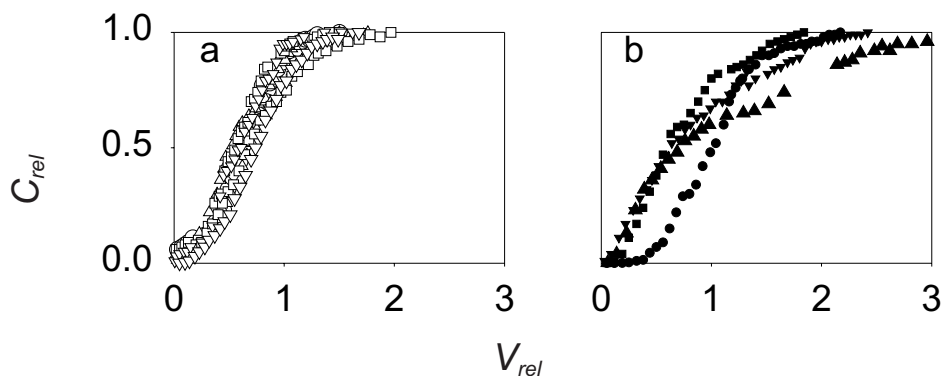

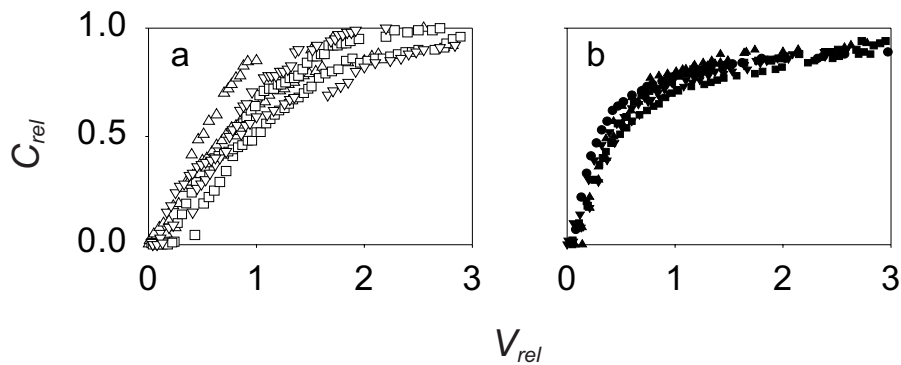**Fig. 4.** Chloride breakthrough curves in southern chernozem cores (a) before and (b) after the pulse of $CaCl_2$ +NaCl.

Fig. 5. Chloride breakthrough curves in chestnut soil cores (a) before and (b) after the pulse of $CaCl_2$ +NaCl.

as compared with the transport, and sodium did not have enough time to enter the cation exchange complex. More time was available for cation exchange on the slow-flow experiments. A similar effect was observed for uranium transport (Barnett *et al.*, 2000).

Data on the concurrent transport of Cl, Ca and Na are shown in Figs 6 and 7. The data come from the late phase of the experiments, when the last pulse was monitored after about 22 and about 30 pore volumes of Ca-containing solutions for the chernozem and chestnut soils, respectively. Up to 16 pore volumes of 0.001N $CaCl_2$ solution passed the columns during this phase of the experiment. In chestnut soil, the breakthrough curves of Cl, Na and Ca ions can be grouped by the flow rates rather than by the specifics of their interaction with surfaces in the soils (Fig. 6). Changes in flow rates seem to cause changes in the relative input of different groups of pores in the total transport in the chestnut soil. The Cl ion approaches the equilibrium levels slightly slower than Na. In the chernozem samples, the differences

between chloride and sodium transport are visible even better (Fig. 7). Leaching of sodium occurs as if it is available for leaching only in a relatively small part of pore space. A larger part of pore space, including fine pores, is available for the chloride transport, and that causes a slower approach of the effluent concentration to the influent one. The relatively fast leaching of sodium also shows that the kinetics of ion exchange is relatively fast as compared with the ion transport.

The physical and chemical properties in Table 1 do not explain the differences in the Cl, Ca, and Na transport in the two soils under study. The chernozem soil exhibits more aggregation and its bulk density is less than the chestnut soil. These structural differences impact transport. In the chernozem soil, the presence of large pores provides the accessibility of the cation exchange complex for ions in moving soil solution, and the large mobile soil solution proportion than in chestnut soil. The compacted chestnut soil has a pore structure in which pore surfaces can rapidly become Ca-saturated.
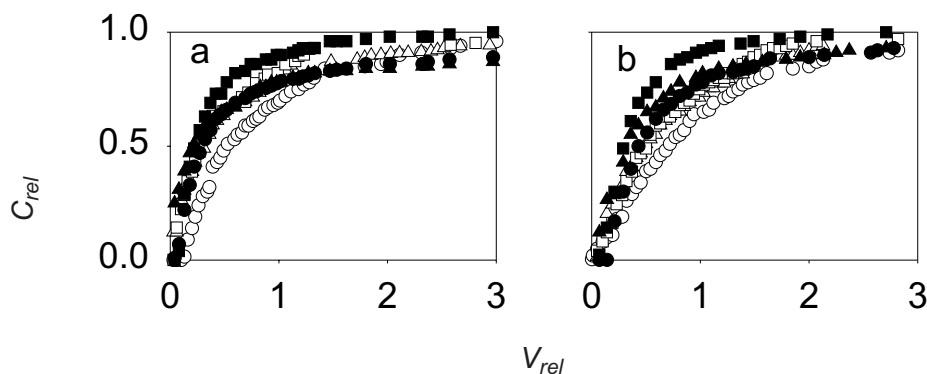

Fig. 6. Chloride ($\bigcirc$, $\bullet$), calcium ($\triangle$, $\blacktriangle$) and sodium ($\square$, $\blacksquare$) breakthrough curves observed in slow-flow (hollow symbols) and fast-flow (filled symbols) experiments with two chestnut soil cores.
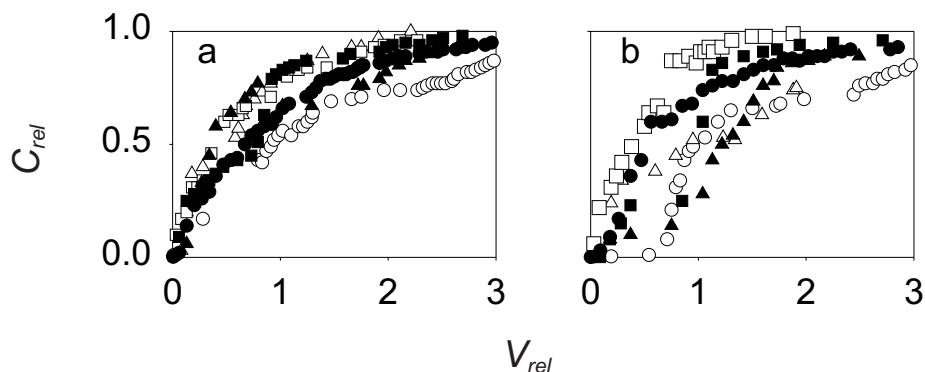
Fig. 7. Chloride (○, ●), calcium (△, ▲) and sodium (□, ■) breakthrough curves observed in slow-flow (hollow symbols) and fast-flow (filled symbols) experiments with two southern chernozem soil cores.

CONCLUSION

The physical heterogeneity governed the transport of ions in this work. This heterogeneity may cause fast transport of reactive pollutants in soil profiles, groundwater pollution, and creates a challenge of incorporating the physical heterogeneity into models of pollutant transport in soils and sediments.

ACKNOWLEDGMENT

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