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Solute Transport in Undisturbed Silt Loam Soil Columns with Preferential Path

Ting Yang[1], Beibei Zhou[1,2]* and Quanjiu Wang[1,2]*

[1]Institute of Water Resources and Hydro-electric Engineering,
Xi'an University of Technology, Xi'an, 710048, China.
[2]State Key Laboratory of Soil Erosion and Dryland Farming on the Loess Plateau,
Institute of Soil and Water Conservation, Northwest A.F University, 712100, Yangling, China.

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Solute transport of chemicals, especially of heavy metal ions, in soil often causes unexpected groundwater contamination in China because of preferential flow paths. Consequently, there is interest in predicting the solute mobility in agricultural soils on the extensive Loess Plateau. In this study, the effects of different chemicals including a conservative anion (Cl^-), a heavy metal ion (Cu^{2+}) and a fertilizer ion (NO_3^-) on solute transport were studied in an undisturbed, saturated, silt loam soil column using a series of miscible experiments. Two controlled situations were applied: solute application method (small pulse. large pulse, duration pulse) and pore water velocity (slow 1.47 cm/h, fast 3.34 cm/h). The chloride transport process in the soil columns were simulated with two-flow region model. Results indicated that: (1) the breakthrough curves (BTCs) for different input methods varied greatly but bimodal pumps were present for both small and large pulse inputs. (2) the pump value appeared later with the increase in solute input time. (3) asymmetry and tailing of BTCs increased for the same input method when pore water velocity was increased. (4) pump values for the fast flow velocity were higher than those for the slow velocity for large pulse BTCs. (5) breakthrough time advanced with increasing pore water velocity, and was not dependent on the input method. and (6) shapes of BTCs for Cl^- and NO_3^- were similar, showing both asymmetry and bimodal pumps but the pump value was notably different. However, Cu^{2+} behaved differently from the anions under the same input method conditions and its relative concentration was much lower. Both small and large pulse breakthrough curves could be accurately fitted by the two-flow region model.

Key words: Breakthrough curves, pore water velocity, solute application method, ions, two-flow region model.

With the continuing increase in the global human population and the problems [1] with ensuring sufficient supplies of food to feed it, various measures have been used in irrigation and fertilizer management in order to improve soil productivity. However, inappropriate practices in the application of irrigation and fertilizer have sometimes caused serious secondary salinization, which has reduced the area of available productive farmland. This has motivated numerous experiments and theoretical studies relating soil properties to soil water movement and chemical transport.

Kluttenberg and Horton (Kluttenberg *et al*., 1990) studied water and solute movement in soil and showed that, in soils containing macropores, both water and solutes can move preferentially through the macropores bypassing much of the soil matrix. The effect of preferential

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* To whom all correspondence should be addressed.
Prof. Zhou Beibei, Prof. Wang Quanjiu, Institute of Water Resources and Hydro-electric Engineering,
Xi'an University of Technology
E-mail: happyangle222@yahoo.com.cn;
wquanjiu@163.com.

flow on water and solute transmission has been widely studied in soils outside of China. The term preferential path refers to noncapillary pores and channels formed by biological and nonbiological activities (Luxmoore, 1981). A description of soil macropore features and their influence on water and chemical movement through the soil profile can be obtained through miscible displacement experiments. For example, Nielsen and Biggar (Nielsen *et al.*,1962) studied the effect of hydrodynamic dispersion and diffusion of a tracer chemical on the solute transport in their early work, and found that microscopic flow velocity distribution affected breakthrough curves (BTC). Jardine *et al.* (Jardine *et al.*,1993) conducted a miscible displacement experiment using reactive and nonreactive tracers in large undisturbed soil columns that contained pores larger than 0.3 mm in diameter. Niu *et al.* (Niu *et al.*, 2005) studied the intrinsic processes driving preferential flow, and showed that the soil matrix had a significant influence on water transport. Zhu *et al.* (Zhu *et al.*,1998) studied the effect of pore water velocities on the transport of tritium in soil and found that dispersion increased with the increase of pore water velocity. Ji *et al.* (2009) studied the effect of different physical and chemical factors on the transport of heavy metals in soil. The results showed that the first peak value (the largest solute concentration) significantly increased in conditions having multi-components compared with those having single components. Furthermore, increased ionic strength could facilitate the transport of heavy metals and decrease their retention in the columns. However, little research on the multiple factors affecting BTCs in Loess Plateau soils has been reported, along with the deleterious effects on the environment. Thus, the objective of this study was to identify the characteristics of BTCs in a loessial soil when using different input applications, pore water velocities and tracers.

MATERIALS AND METHODS

Undisturbed soil columns were excavated from the A and B horizons (10–60 cm depth) in the Changwu field station, Shaanxi Province, on the Loess Plateau of China. The soil is a loam (United States Department of Agriculture generic soil classification system); the particle size distribution was determined by sieving in combination with the pipette method (Shao *et al.*, 2006) (Table1).

Table 1. Particle compositions of the studied soil

Sampling depth (cm)	Sand (%) (50-2000 µm)	Silt (%) (2-50 µm)	Clay (%) (<2ìm)	Textu-ral Class
0-10	43.490	48.397	8.131	loam
10-20	34.973	60.053	4.974	silt loam
20-30	29.366	55.889	14.745	silt loam
30-40	41.422	51.176	7.402	loam
40-50	41.822	50.937	7.241	loam
Mean	38.215	53.287	8.498	loam

Before conducting a miscible displacement experiment, molten paraffin wax was poured down the inner walls of the soil column in order to coat them thereby eliminating the boundary effect. The saturation of each soil column was achieved by using a Mariotte bottle to supply water to the base of the column for about two weeks. The saturated hydraulic conductivity was then determined by supplying the water continuously to the top of the column until the value of the saturated hydraulic conductivity was constant. Then the other end of the soil column was also capped with a filter disc made from quick setting porous cement (Booltink *et al.*, 1991), which had an inlet in the center as shown in Figure 1. The inlet at the top of the column was connected to a peristaltic pump, which controlled the input water velocity and solution pulse time, while the effluent from the outlet at the bottom of the column was collected in a 500-ml volumetric flask.

Each column was subjected to two pore water velocity (1.47 cm/h, 3.34 cm/h) treatments, which were controlled by a piston pump. Three types of breakthrough curves were generated for each column in sequence. The first type was a chloride BTC, referred to as “small pulse”, generated by introducing 0.1 pore volumes of solution (0.15 mol/L of KCl and 0.4 mol/L of $Cu(NO_3)_2$ at the low pore water velocity rate (1.47 cm/h), and then recovered by using about four pore volumes of deionized water. The second type of chloride BTC, denoted as “large pulse”, used a pulse of about 1 pore volume generated in the same way as the small pulse. Finally, a duration solution input experiment was conducted. After carried these three solute applications, higher pore water velocity (3.34 cm/h) was used in the same way. The chloride (Cl^-) concentration of the effluent was determined by titration with silver nitrate solution (0.01 mol/L); potassium (K^+) concentration by flame photometer; nitrate ion(NO_3^-) concentration by ion chromatography; and copper (Cu^{2+}) concentrations by uv-vis spectrophotometry.

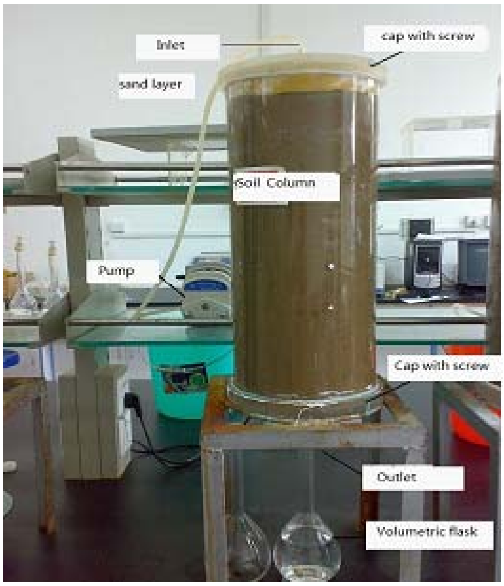

Fig. 1. Experiment set up for measuring solute flow through an undisturbed silt loam soil column

After collecting the data, we fitted the results using the two-flow region model which simulate the two-peak breakthrough curves more accurately. The model divided soil water into two regions based on their flow velocity. Both water regions had a non-zero flow rate. Without loss of generality, we denoted the fast flow region as A and the slow region as B. The soil system was characterized by the pore water velocity (V_A, V_B), water content (θ_A, θ_B)ÿsolute concentration (C_A, C_B), the dispersion coefficient (D_A, D_B). The two domains were related by an interaction term Γ such that:

$$\Gamma = \alpha(C_A - C_B) \qquad ....(1)$$

The convection-dispersion equation in the two domains to give their respective mass transfer coefficients could be expressed as (Skopp *et al.*, 1981).

$$\frac{\partial C_A}{\partial t} = D_B \frac{\partial^2 C_A}{\partial x^2} - V_A \frac{\partial C_A}{\partial x} - \frac{\alpha}{\theta_A}(C_A - C_B) \qquad ...(2)$$

$$\frac{\partial C_B}{\partial t} = D_A \frac{\partial^2 C_B}{\partial x^2} - V_B \frac{\partial C_B}{\partial x} - \frac{\alpha}{\theta_B}(C_B - C_A) \qquad ...(3)$$

where α is the first-order transfer coefficient between the two water flow domains. The initial and boundary conditions for the fast ($i - A$) and slow ($i = B$) flow domains were:

$$C_i = 0 \quad t = 0 \quad 0 < x < L \qquad ...(4)$$

$$V_i C_0 = -D_i(\partial C_i / \partial x) + V_i C_i$$

$$x = 0 \qquad 0 < t \leq t_p \qquad ...(5)$$

$$0 = -D_i(\partial C_i / \partial x) + V_i C_i \qquad t > t_p \qquad ...(6)$$

$$\partial C_i / \partial x = 0 \quad x = L \quad t > 0 \qquad ...(7)$$

By introducing the following ratios:

$f = \frac{\theta_A}{\theta}$ and

$$\gamma = \frac{V_A}{V_B} \qquad ...(8)$$

θWe obtained:

$V = fV_A + (1 - f)V_B$ and

a v=3.34cm/h
b v=1.47cm/h

$$C = \frac{C_A f\gamma + C_B(1 - f)}{f\gamma + (1 - f)} \qquad ...(9)$$

Where is the total volumetric water content, is the mean pore water velocity(cm/h), and C is the mean solute transport concentration($\mu g/ml$). Moreover, andwere assumed to be linear functions of and, respectively (Skopp *et al.*, 1981):

$$D_A = D_0 + \lambda V_A \text{ and } D_B = D_0 + \lambda V_B \qquad ...(10)$$

Whereis the dispersivity (cm) and D_0 is the molecular diffusion in water (cm²/h).

RESULTS AND DISCUSSION

The effect of different pulse applications on chloride BTCs

Since chloride tracer is stable and non-absorbable, we chose its BTCs to study the effect of different pulse applications. The BTCs under three different application methods were shown in Figure 2. For all the miscible displacement experiments, BTCs under the three applications were observed, which initially increased sharply and then reached equilibrium or displayed one or two pump values. The pump value appeared much later with increasing solute input time, as shown in Figure 2a: the duration pulse came to equilibrium at about 1.7 pore volumes, the large pulse application exhibited its first peak at 1.2 pore volumes, and the first peak position exhibited by the small pulse input was at about 0.5 pore volume. By using the same pore water velocity in one column, the effect of soil structure could be ignored, and thus, diffusion was the main factor inducing this phenomenon. It is apparent that one tracer had a greater diffusion coefficient than the other, and not only invaded the immobile zones but also diffused down the column more rapidly than the other tracer. Therefore, we noted that the tracer of the small pulse appeared in the effluent earlier than those of the large and the duration pulses (Figure 2). This diffusion effect for the three pulse applications was in the following order: small pulse > large pulse > duration pulse. However, results obtained from Figure 2b showed that the appearance time of the pump value was different from that in Figure 2a, the small pulse reached its peak at about 0.9 pore volumes, while the large pulse peak was at about 1.2 pore volumes. This shows that different flow velocities resulted in different appearance times. In Figure 2a, most of the chloride had move through the soil column at the very first 1.5 pore volumes at the higher flow velocity. This was much faster than that in the case of the slower flow velocity (Figure 2b), which suggested that a greater portion of the chloride solute had moved through the macropores, which more rapidly transported it in this case (Bouma *et al*., 1978, Cassel *et al*., 1974; Elrick *et al*., 1966).

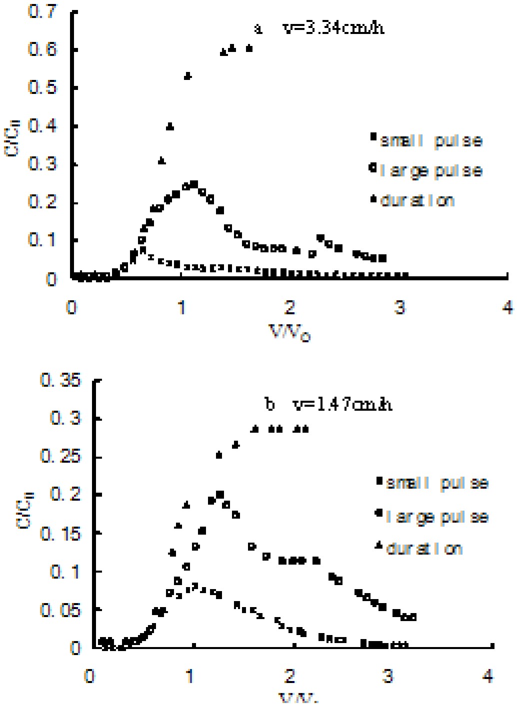

Fig. 2. Breakthrough curves of different pore water velocities (v) with three pulse applications respectively; a small pulse application; b large pulse application; c duration pulse application

The BTCs in Figure 2 showed that bimodal pumps were obtained in the pulse application experiment. Both in the small and large pulse experiments, the first pump value was about two times larger than the second pump value in all the BTCs, and the difference observed in the large pulse experiment was much larger than that seen in the small pulse experiment. Hornberger *et al.* (1990) studied solute transport in macroporous forest soils and concluded that solutes could move through macropores and other preferential flow channels in forest soils when solute input rates at the surface were high enough, and that significant macropore flow always occurred in the soil block. Despite the importance of macropore flow, the fractional volume of the total pore water that participated in solute transport decreased only slightly with increasing flow rate. Ma and Selim (1995) studied undisturbed soil columns under different flow velocities and obtained bimodal pump values that indicated that dual porosities existed in the soil. According to Li and Ghodrati (1997) most of the solute was transported through the macropores at a higher rate and appeared in the effluent earlier, while the remainder of the solute mass was transported through the soil matrix at a lower rate, which resulted in the second pump value on the tailing side of the BTC.

The effect of different pore water velocities on BTCs

The effect of different pore water velocities on chloride BTCs with three input applications are shown in Figure 3. It is evident that pore water velocity had a great effect on the BTCs, both on the breakthrough time and the pump value. In Figure 3a, for the small pulse application experiment, with the increase in pore water velocity, an earlier breakthrough was found in the chloride transport, where the first pump value occurred within less than 0.5 pore volumes at the higher pore water velocity; when the pore water velocity was decreased to 1.47 cm/h, the first pump value was a little higher and occurred much later. In contrast, for the large pulse in Figure 3b, the pump value changed more notably, being greater for the higher pore water velocity. When the pore water velocity was 1.47 cm/h, the first pump value appeared at about 1.3 pore volumes. When the pore water velocity was increased to 3.34 cm/h, the first pump value occurred at 0.3 pore volumes, which was much earlier than that found with the low pore water velocity. This was assumed to result from the changes in both the solute mass and the pore water velocity. It indicated that increasing the pore water velocity resulted in relatively greater solute transport occurring through the macropores with correspondingly less dilution of the solute by the deionized water used to subsequently wash it from the columns. Nkedi-Kizza *et al.* (Nkedi-Kizza *et al.*,1983) obtained similar results. Li and Ghodrati (Li *et al.*, 1997) also found that, when the flow rate was increased to two times the saturated hydraulic conductivity, greater amounts of a nitrate tracer would enter the macropore system where it would spend a much shorter time before arriving at the bottom of the soil column, while the remaining tracer had to diffuse through the soil matrix. The distance between the peaks of the bimodal pump obtained in the small and large pulse experiment is obviously different. Zhou *et al.* (Zhou *et al.*, 2011) studied chloride transport in undisturbed soil columns of the Loess Plateau and noted that, in large pulse applications, the distance between the first and the second peaks did not change much with changes in pore water velocity, but changed notably in the small pulse experiment. Figure 3 shows similar results.

All the BTCs, it was found that: all the BTCs displayed double pumps and the position of the two pumps varied not only with the mass of the tracer but also with the flow velocity. Moreover, the shapes of the BTCs for the smaller pore water velocity tended to be more symmetric than those for the larger pore water velocity. This was due to the greater amount of chloride that diffused into the matrix and was transported at a velocity similar to that of the homogeneous system thereby reducing the chloride concentration. The results from the small pulse in Figure 3a were qualitatively similar to those from the large pulse in Figure 3b. With the increase of the pore water velocity, greater asymmetry in the BTC occurred, reflecting the earlier breakthrough and greater degree of tailing. Since greater amounts of chloride were transported through the column more rapidly at the high pore

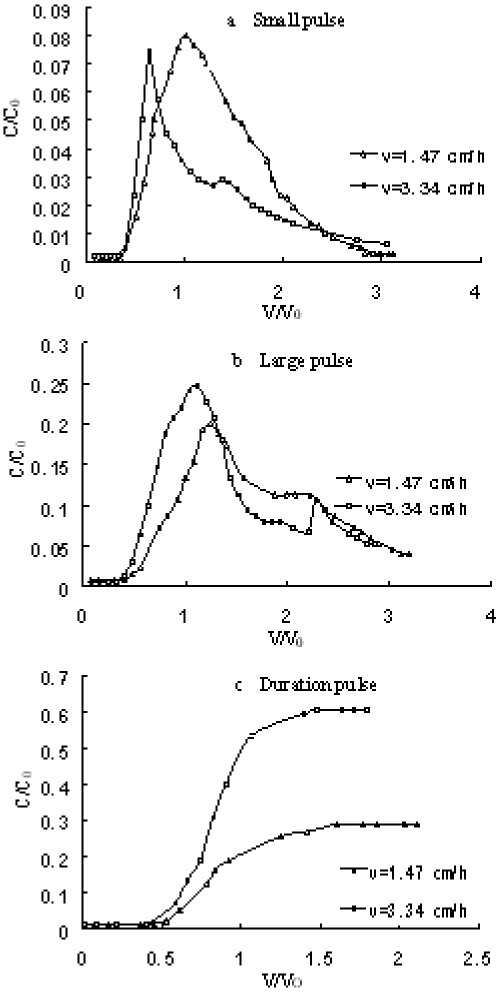

Fig. 3. Breakthrough curves of different pore water velocities (v) with three pulse applications respectively; a small pulse application; b large pulse application; c duration pulse application

water velocity, a lesser amount of the chloride solute diffused into the soil matrix (Bouma 1977, Sollins *et al*., 1988). However, there were also notable differences between the two treatments. The change in asymmetry of the BTCs for the large pulses in Figure 3b was less than for the small pulses in Figure 3a; and the relative concentration of chloride at 3.34 cm/h was distinctly higher than that at 1.47 cm/h in the large pulse case, whereas it was not when small pulses were used.

In the duration application experiment, the concentration of the solution increased with the pore volumes until reaching a constant value. The shapes of all the BTCs displayed an S-curve. When the pore water velocity was 1.47 cm/h, the relative chloride concentration increased to 0.3 more slowly than when the pore water velocity was 3.34 cm/h and the relative concentration was close to 0.7 (Figure 3c). The phenomenon indicated that more tracers would be transported more slowly through the soil matrix and diffused freely throughout the soil columns when pore water velocity was lower, but the solution tended to be transported much faster in the effluent and diffusion was less at the higher pore water velocity.

The effect of different tracer ions on BTCs in the small pulse experiment

Figure 4 shows that the BTCs of different tracers varied in the small pulse experiment for the pore water velocity of 3.34 cm/h. This was due to the differences in the properties of the tracers. As noted in the previous sections, the chloride BTC in Figure 4a displayed asymmetry with an early breakthrough and a long tailing, and had two pumps. The shape of the nitrate BTC was very similar to that of the chloride BTC. Both chloride and nitrate had an early breakthrough at about 0.8 pore volumes. However, the relative concentration values of the nitrate BTC were much lower than those of the chloride BTC. This may be attributed to the characteristics of these anions. Chen *et al.* (Chen *et al*., 2000) investigated the effect of the cation species associated with nitrate ions on the transport characteristics of nitrate ions in the soil environment. They obtained BTCs using $Ca(NO_3)_2$ and KNO3 tracers and found that the relative concentration values of nitrate ions when using $Ca(NO_3)_2$ as a tracer were higher than those when using KNO_3. They attributed this effect to differences in the characteristics of monovalent and divalent cations. Li and Ghodrati (1997) also confirmed the rational behind the observed nitrate BTC behavior in this study by showing that nitrate often did not breakthrough until 0.8 pore volumes, and that all the nitrate had leached out within 1.3 pore volumes of leachate. This was very similar to the findings shown in Figure 4a.

The shape of the copper BTCs differed greatly from, and the concentrations in the effluent were much lower than, those for the other three ions (Figure 4b). This was primarily attributed to intense adsorption by the soil. Copper is a heavy metal ion and its bioavailability and mobility in soils mainly depends on redistribution processes between solution and solid phases and among solid-phase components (Han *et al*., 2003). This means that the copper transport in soil is a more complicated process than in the case of the other studied ions.

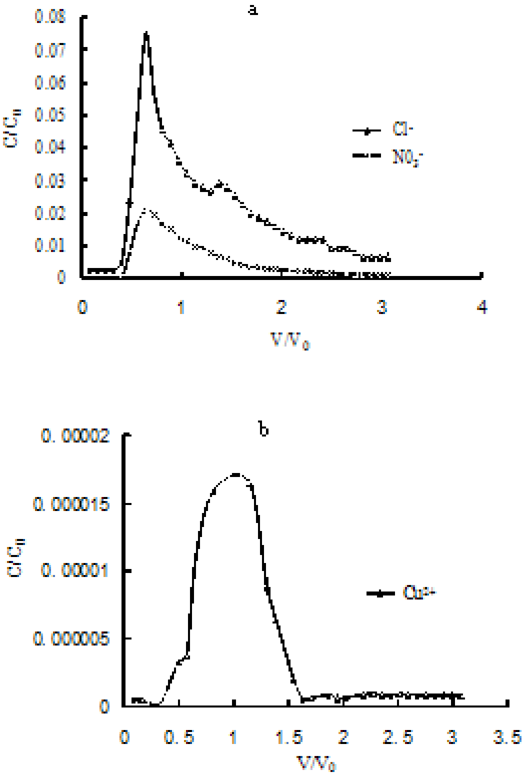

Fig. 4. Breakthrough curves of different transport ions with a small pulse input; v=3.34cm/h

The effect of different tracer ions on BTCs in the large pulse experiment

Figure 5 shows the BTCs of different ions in the large pulse experiment that used a pore water velocity of 3.34 cm/h. The BTCs of chloride and nitrate were found to be more similar in the large pulse input method (Figure 5a) than those in the small pulse experiment. All the BTCs had bimodal pumps that occurred at the same pore volumes, and early breakthroughs occurred at about 1 pore volume. The first pumps were much larger than the second one, which means that most of the chloride and nitrate was transported through the macropore system whereas only a small portion was carried through the soil matrix. Li and Ghodrati (Li *et al.*, 1997) studied the effect of water flux rate on BTCs in the field. They found an equal double-pump curve was obtained at a relative flux that was 0.75 times the saturated hydraulic conductivity. The result suggested that the macropore system and the soil matrix were equally involved in the nitrate transport process. However, when the flux was increased to the saturated hydraulic conductivity of the matrix, the macropore system dominated the transport process and the BTC had dissimilar double pumps with the first pump being higher than the second. Both the Changwu loam soil, used in this presented study, and the silt loam soil, used by Li and Ghodrati (Li *et al.*, 1997), exhibited bimodal pumps when the pore water velocity was close to the saturated hydraulic conductivity. Since chloride is similar in behavior to nitrate to some extent, it has been suggested that, in some circumstances, results obtained from research on chloride transport could also be used to deduce nitrate transport instead of conducting actual nitrate transport experiments (Sun *et al.*, 2004). However, the relative concentrations of nitrate in the effluent were lower than those of chloride (Figure 5a), thus adsorption rates were assumed have an effect on nitrate transport.

In contrast to chloride and nitrate, a BTC having multiple pumps was obtained for copper transport in the soil (Figure 5b). According to Hoehn *et al.* (Hoehn *et al.*,1988), Moreno and Tsang (Moreno *et al.*,1991) and Nordqvist *et al.* (Nordqvist *et al.*,1992) multiple-pump BTCs have been reported for tracer movement in fractured media. The tracer was believed to migrate to fractures near the injection point where it could move more rapidly but tracer that could not enter fractures had to follow small pathways where movement was slower The differences in travel time of the tracer between the injection point to the various fractures or to the outlet resulted in multiple pumps (Li and Ghodrati, 1997). Copper breakthrough in the soil is a complex mechanism that may alter the soil structure and lead to the production of the multiple pumps. Ji *et al.* (2009) studied the transport of heavy metals in porous media using numerical simulation and compared transport characteristics of four heavy metals under various soil conditions. The capacity of soil to absorb the heavy metals increased with increasing soil pH, while the adsorption of copper decreased with increases in sodium concentration. Competition for adsorption occurred among hydrogen, sodium and copper ions that reduced the capacity of soil for copper. Since, in this study, neither the soil pH was neutral or the sodium concentration in soil was zero, the adsorption capacity of the soil for copper was high, leading to the much lower relative concentration of copper in the effluent.

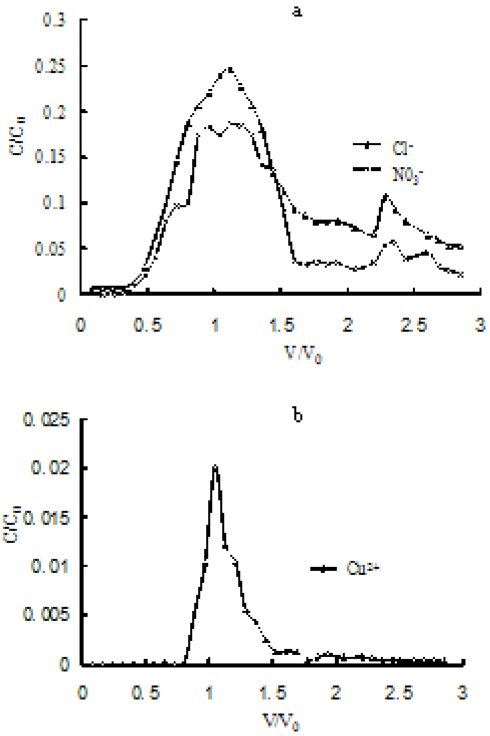

Fig. 5. Breakthrough curves of different transport ions with a large pulse input; v=3.34 cm/h

Effect of pore water velocity on chloride breakthrough parameters

To further study the effect of preferential solute transport on the BTCs, we used the two-flow region model to fit both small and large pulse experimental data of chloride. As shown in Figure 6 and detailed in Table 2, the two-flow region model was able to characterize the BTCs, especially in accurately fitting the experiment data.

Table 2. Parameters of fitted two-flow region model parameters for the large pulse application method

Model	V cm/h	SSQ (x 10-2)	λ cm	D cm^2/h	α	V	f
Two-flow region model	3.34	3.98	0.41	1.49	0.0023	2.113	0.513
				1.00	±0.0003	0.018	0.021
	1.47	1.27	0.63	1.12	0.0026	2.690	0.507
				1.79	±0.002	0.22	0.016

* v, pore water velocity; λ, the values of dispersvity; D, dispersivity coeffiecient; α, mass transfer coefficient; y, relative magnitude; f, the fast flow partition coefficient.
* Mean particle density was determined to be $2.65g/cm^3$
* refer to mean standard error.

Because the small pulse breakthrough curve is just for model validation, the parameters fitted from the large pulse were considered (Ma *et al.*, 1995). The dispersivity, λ (cm), is an indication of the distance traveled by the solute and is, therefore, directly related to the tortuosity of the flow path. The values of λ were calculated from the fitted dispersion coefficient D values (Eq. 10). The calculated values of the dispersivity indicated that the solute transport paths were much more torturous. The dispersion coefficient increased with the decrease in pore water velocity (Table 2).

Van Genuchten and Dalton (Van *et al.*,1986) and Schulin *et al.* (Schulin *et al.*, 1987) stated that, for any two or more pore geometries,

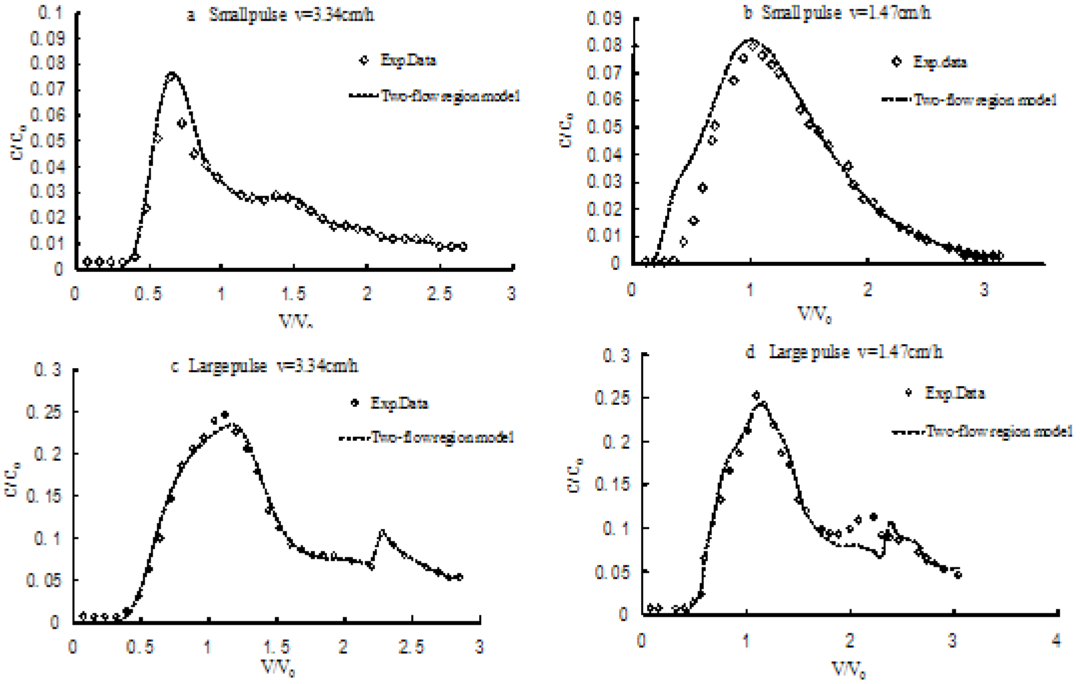

Fig. 6. The two-flow region model simulated breakthrough curves of both small and large pulses with different pore water velocities (v)

the differences in the mass transfer coefficients depends not only on the pore space geometry, the solute diffusivity, and the relative magnitude of the mobile region, but also on the pore water velocity. In our experiment, the values of the mass transfer coefficient decreased with the increase in pore water velocities, which would enhance the development of double BTC peaks. Ma and Selim (1995) studied a disturbed soil column and found that, with an increase in pore water velocity, less solute exchange between the two-domains occurred. Griffioen *et al*. (Griffioen et a., 1998) examined published data and found that the dominant trend was a linear variation of the transfer rate with the mobile fluid velocity.

As the fast flow partition coefficient, f, approaches 1, the contribution of the slow region to solute transfer becomes negligible and the resulting BTC approaches symmetrically unimodal distribution. In our study, the relative contributions of the two flow domains were similar, as indicated by the values close to 0.5, and resulted in asymmetric BTCs (Table 2).

The relative magnitude of flow velocity in the two-flow region model (γ) also affects the shapes of the dual peaks. If γ =1, or was almost equal to 1, the two-flow region model could be reduced to a one-region model and no double peaks would be expected. However, as shown in Figure 6 and Table 2, for our soil column experiments values of y were larger than 1 and, therefore, double peaks BTCs were obtained. The decrease in pore water velocity resulted in an increase in the value of γ from 2.113 to 2.690. Further decreases in pore water velocity would result in increases in γ and eventually the double peaks would become two separate peaks. Ma and Wang (2004) observed this effect when ã reached a value of 10 in their laboratory experiment and the double peak disappeared.

DISCUSSION

In this study, the results showed that preferential flow occurred in an undisturbed silt loam soil column at controlled fluxes. The contribution of input methods to the preferential flow increased with increases in solute mass. Bimodal pumps were obtained from both small and large solute pulse inputs. An S-shape BTC was observed in the duration application experiments. Increasing pore water velocity increased the asymmetry of the BTCs, which had an earlier breakthrough and longer tailing. These were especially notable for the small pulse input experiments.

The shapes of the BTCs of the three different ions varied notably. The BTCs for chloride and nitrate were very similar, but the relative concentration values of nitrate in the effluent were lower than those of chloride. Copper BTCs differed greatly from those of the anions and the relative concentration values of copper were much lower than those of the anions due to strong adsorption within the soil matrix. The two-flow region model characterized the BTCs and accurately fitted the experimental data. The dispersion coefficient, mass transfer coefficient and the relative magnitude of flow velocity increased with the decrease in pore water velocity. In our study the relative contributions of the two flow domains were similar, as indicated by the values close to 0.5, and resulted in asymmetric BTCs.

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