

Experimental study on preferential solute transport in a Loess Plateau soil

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Abstract

In soils of the Loess Plateau containing macrospores, both water and solute transport can move preferentially, bypassing much of the soil matrix. The objective of this study was to examine the effect of solute input methods with small pulse input and large pulse input and four pore water velocities on preferential solute transport through undisturbed loessial soil columns collected from the Loess Plateau. Chloride breakthrough curves (BTCs) were generated using the miscible displacement method under water-saturated, steady flow conditions. Using the same column, 0.15 mol L⁻¹ CaCl₂ solution was added, first in a small pulse (0.1 pore volumes) and second, after recovery, a large pulse (0.5 pore volumes). The convection-dispersion equation (CDE) and the two-region model (T-R) were used to describe the BTCs, and their prediction accuracies were compared. All the BTCs obtained for the different input methods and the four pore water velocities were all smooth and had a single-peak. However, the shapes of the BTCs varied greatly; small pulse inputs resulted in more rapid attainment of peak values that appeared earlier with increases in pore water velocity whereas large pulse inputs resulted in an opposite trend. Both models could fit the experimental data well, but the prediction accuracy of the two-region model was better. The values of the dispersivity, λ , calculated from the dispersion coefficient obtained from the CDE were about one order of magnitude larger than those calculated from the dispersion coefficient given by the two-region model, but the calculated Pelect number, Pe , was lower. The mobile-immobile partition coefficient, β , decreased while the mass exchange coefficient increased with increases in pore water velocity.

Keywords: solute transport; CDE; two-region model; pore water velocity.

Abbreviation: BTCs, breakthrough curves; CDE, convection-dispersion equation; T-R, two-region model; SSQ, sum of squares residual value; Exp., experimental.

Introduction

Investigations of water and solute movement in soil where macropores exist have shown that preferential flow occurs through the macropores resulting in large parts of the soil matrix being bypassed (Thomas and Phillips, 1979; Beven and Germann, 1982; White, 1985). Macropores are formed by biological channels and soil structural voids, and field and laboratory studies have demonstrated the importance of the macropore system when considering water and solute transport (Bouma and Anderson, 1977). Macropores can have a great effect on water and solute transport in the soil even though they may comprise only a small proportion of the total soil pore system (Coats and Smith, 1964; Desmedt, 1979). Under certain conditions, water and solutes may enter the soil macropore system, bypass the soil matrix and rapidly reach lower depths of the soil profile or the groundwater table, which results in pollution of underground water reserves. Thus, for example, pesticides have been detected in many aquifers as well as in surface waters as a result of agricultural practices. Furthermore, rapid non-uniform leaching via preferential flow paths is more likely to result in a fraction of the contaminant percolating into the groundwater before it can either degrade or be adsorbed within the soil matrix (Stagnitti et al., 1994).

Laboratory studies conducted with columns of undisturbed soil material have been used to examine the dependence of preferential water and solute transport on soil structure (Kanchanasut et al., 1978), soil texture (Bouma and Anderson,

1977), soil water content (Elrick and French, 1966), initial soil water content (White et al., 1986) and rates of water and solute application (Seyfried and Rao, 1987). Less research has been undertaken to examine the effect of the solute application method and of the pore water velocity on subsequent preferential movement of the solute. This question is pertinent to the formulation and validation of transport models for preferential flow and is relevant to water and chemical management. And the detection of preferential flow in soils is commonly achieved by applying a chemical tracer to the soil surface and measuring its concentration over time at a certain depth to produce a breakthrough curve (BTC) (Haws, Das et al., 2004). On the Loess Plateau, the existence of macrospores in the soil may create preferential flow paths. The flow through macrospores can rapidly move surface-applied agricultural chemicals through the macrospores, resulting in economic losses and posing an environmental hazard. An understanding of preferential flow processes is needed in order to predict the movement of agricultural chemicals through the soils of this region and to improve techniques for managing the application of such chemicals. The objectives of this study were: (1) to examine the effect of solute input methods and pore water velocity on preferential solute transport in loessial soil columns and (2) to evaluate the convection-dispersion equation (CDE) and the two-region model for predicting non-reactive solute breakthrough curves (BTCs) for loessial soil.

Results and discussions

Effect of pore water velocity on breakthrough curves for small pulse input applications

Figure 1 presents the small pulse BTCs with pore water velocities of 3.34, 4.18, 6.69, 8.35 cm h⁻¹ using 0.15 mol L⁻¹ CaCl₂ solution as a tracer. All the BTCs for the different pore water velocities were smooth and had a single peak. The chloride concentration first increased and then decreased with increasing pore volumes of effluent. From Fig. 1, it can be clearly seen that pore water velocity had a considerable effect on the BTCs. With increasing pore water velocity, most of the chloride ions reached the base of the soil column more rapidly. This resulted in different degrees of dilution when leaching with solution 0.005 mol L⁻¹ CaCl₂, such that the concentrations of chloride ion generally increased as the pore water velocity increased. Similarly, increasing the pore water velocity increased the peak values of the chloride BTCs. The BTCs also showed more evident tailing characteristics for the slower pore water velocities (Fig. 1). This was likely due to the slower movement of some of the chloride solution through the soil matrix by convection and diffusion. Thus, a fraction of the ions in the pulse flowed relatively rapidly via the macropores to the base of the soil column while the remaining ions migrated through the soil matrix relatively slowly by diffusion, which led to the emergence of ions in the effluent over a longer period of time as demonstrated by the long tailing. The degree of tailing for the slower pore water velocities can thus be considered to result from a lesser degree of bypass flow and a greater degree of flow through the soil matrix (Bouma and Anderson, 1977; Sollins and Radulovich, 1988) resulting in an overall slower solute flow. With increasing pore water velocity, the chloride ions moving by diffusion cannot fully exchange with ions by convection while a greater fraction move through preferential flow so that the tailing becomes longer. This explanation is consistent with our experimental results. Notably, there was no secondary pump value observed on the tailing side in our experiments.

Effect of pore water velocity on breakthrough curves for large pulse input applications

Figure 2 presents the large pulse BTCs with pore water velocities of 3.34, 4.18, 6.69, 8.35 cm h⁻¹ using 0.15 mol L⁻¹ CaCl₂ solution as a tracer. The BTCs all show that the concentration of chloride ions initially increased to a peak value shortly after the pulse was applied and then decreased with increasing pore water velocity. All of the BTCs were smooth and had single peaks, which was similar to the small pulse input BTC cases. The maximum concentration values indicated that some of the chloride solution moved rapidly through the preferential flow pore spaces mixing little with the initial soil solution. Anderson and Bouma (1977a) and White et al. (1986), using a pulse application of chloride solution, have shown similar rapid increases in chloride concentrations in BTCs for initially drained, undisturbed soil materials. The occurrence of asymmetry in the large pulse BTCs was less obvious than in the small pulse BTCs. This was due to the matrix flow in the miscible displacement process being slow during the pulse, although greater amounts of Cl⁻ entered the matrix, so that it initially had no evident effect on the solute in the effluent. This meant that the primary flow path of the solute initially occurred through the macropore system while the secondary flow was through the matrix. Solute entering the soil matrix caused the solute concentration in the matrix to increase gradually. Subsequently, the solute concentration in the effluent

via preferential flow rapidly declined while the solute concentration in the matrix decreased relatively slowly. The two differing infiltration processes occurring at different rates were the main causes of the asymmetry observed in the BTCs. However, the greater amounts of solute entering the matrix during the large pulse, compared with the small pulse, resulted in higher concentrations of solute in the later effluent samples due to the secondary pathway and this reduced the asymmetry observed in the BTCs. Notably, there was no secondary pump value observed on the tailing side in our experiments.

Impact of different pulses input on, and comparisons between experimental and predicted, breakthrough curves

In order to further study the influences of different pore water velocities on solute transport, chloride BTCs generated by small and large pulse inputs were fitted by both the CDE and two-region model (Fig. 3). All four BTCs showed that the predicted relative concentrations of chloride ions compared favorably with the experimental data (Fig. 3). Therefore, both the CDE and the two-region model could well-describe all the BTCs. All the BTCs for both application methods were smooth and had a single peak (Fig. 3). However, the BTCs varied differently, especially with regard to the peak value, according to the application method. The presence of Cl⁻ in the effluent was detected earlier for the small pulse inputs. It is apparent that the shape of the BTC was dependent on the pulse duration as well as on the pore water velocity. With decreases in pore water velocity, the difference between the peak values of the two application methods became more apparent. The two-region model tended to fit the data better than the CDE, however, the large pulse BTCs were less well-fitted than the small pulse BTCs, and the fit became worse for the large BTCs as pore water velocity increased, especially for the tailing (Fig.3). Although the two-region domain model could describe the process of solute transport better in undisturbed soil than the CDE, the interpretations of individual peaks were not fully satisfactory. Using the superposition principle, Ma and Selim (1994) found that a small pulse BTC contained as much information on solute transport as a large pulse BTC. Column packing and wall effects on preferential flow cannot be completely eliminated and may affect BTCs. Possibly the way in which large and small pores are distributed within the studied loessial soil, as well as the pore water velocity, are important influencing factors that determine whether one or two peaks occur.

Effect of different pulse input methods and pore water velocities on model parameters

In order to further study the effect of pulse input and pore water velocity on the solute transport process, the fitted parameters of the CDE and of the two-region model were examined (Tab.1). In the CDE, the retardation factor, R , was fitted to the BTCs while in the two-region model there were two fitted parameters, i.e. the mobile-immobile partition coefficient, β , and the mass transfer coefficient, ω . From the two fitted models, the Peclet number, Pe , and the dispersivity, λ (cm), were determined from the values obtained for the dispersivity coefficients (Tab.1). Since the processes involved with the large pulse input method were slower, the data obtained from these experiments were used to determine the model parameters, while, the input time was shorter for the small pulse input method, so the data from these experiments was used to assess the prediction accuracy. Therefore, only the effect of pore water velocity on the parameters for the large pulse input method will be discussed.

Table 1. Fitting parameters derived by either the convection-dispersion equation CDE or the two-region model (T-R) in undisturbed soil

Pore water Velocity/cm/h	SSQ		λ		Pe		β		ω	
	CDE	T-R	CDE	T-R	CDE	T-R	CDE	T-R	CDE	T-R
3.34	2.57E-03	7.03E-04	0.23	0.069	185.06	607.27	-	0.19	-	1.66
4.18	2.26E-02	2.14E-03	0.37	0.041	114.00	1014.79	-	0.17	-	1.61
6.69	1.87E-02	7.51E-03	0.65	0.046	64.59	903.47	-	0.082	-	1.87
8.35	1.69E-02	4.38E-03	0.74	0.16	56.75	261.72	-	0.099	-	1.99

Note: SSQ, sum of squares residual; λ , dispersivity (cm); Pe, Peclet number; β , mobile-immobile partition coefficient; ω , mass transfer coefficient

From Table 1, the two models' prediction accuracy in describing solute transport can be compared. The SSQ values indicated that both models predicted values for relative concentrations of Cl⁻ that well-fitted the experimental data. However, in general, the two-region model fits the experimental data slightly better than the CDE. This can be attributed to the greater number of parameters used in the two-region model, which more accurately described the solute transport processes, than those used in the CDE.

Dispersivity, λ

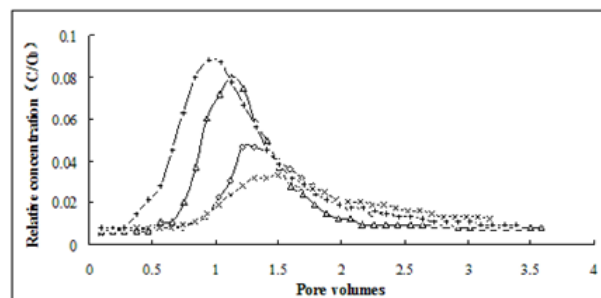
From Table 1, it can be seen that the values of the dispersivity, λ , calculated from the dispersion coefficients given by the CDE were about one order of magnitude larger than those obtained using the dispersion coefficients from the two-region model (Tab.1). The larger λ values result from the definition of D used in the CDE, which is a parameter that combines both dispersion and flow heterogeneity characteristics. The larger λ values also resulted in the more extensive tailing of the calculated BTCs (Fig. 2).

Peclet number, Pe

The Peclet number, Pe , is the ratio of the characteristic times for hydrodynamic dispersion (l^2/D) and convection (l/v_m) and depends solely on the medium, provided the contribution to mixing by molecular diffusion is significant. Thus, Pe provides a measure of the relative importance of advective and dispersive processes. The values of Pe , determined by the dispersion coefficient derived either from the CDE or the two-region model, reflected the inverse relationship between Pe and λ (Tab.1). Comparison of the Pe values in Tab. 1 shows that the Peclet number calculated with Eq. (17) generally followed the same trend for both models (except for 3.34 cm h⁻¹), decreasing with increases in velocity, and hence being largest for the 3.34 cm h⁻¹ by the CDE as well as for the 4.18 cm h⁻¹ by the two-region model. In this study, Pe estimated from the fitted parameters of both models was also sensitive to different degrees, the values predicted by the T-R are much larger than those yielded by the CDE, to the various experimental conditions imposed on the same, or on different columns. The Peclet number provides a measure of the movement of the solute by mass flow moving vertically in the columns, while dispersion involves advective movement and the values obtained indicate that the advective process dominates (Schulin and van Genuchten, 1987). Thus, in all the columns, advective flow was the dominant component of solute transport, especially for the lower velocities (except for 3.34 cm h⁻¹). It appears that even larger velocity impeded diffusive flow more considerable (Tab. 1).

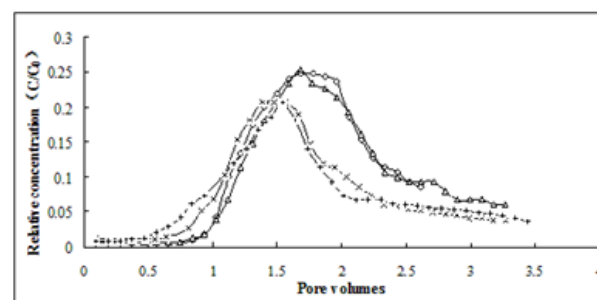
Mobile-immobile partition coefficient, β

The mobile-immobile partition coefficient, β , of the two-region model represents the fraction of solute present in the mobile region under equilibrium conditions (Schulin and van Genuchten, 1987). In the two-region model, solute ions in the



—◇—3.34 cm h⁻¹ —×—4.18 cm h⁻¹ —△—6.69 cm h⁻¹ —+—8.35 cm h⁻¹

Fig 1. Small pulse input, influences of different pore water velocities on BTCs of the experimental result.



—◇—3.34 cm h⁻¹ —×—4.18 cm h⁻¹ —△—6.69 cm h⁻¹ —+—8.35 cm h⁻¹

Fig 2. Large pulse input, influences of different pore water velocities on solute breakthrough curves.

mobile region can freely move by dispersion but can only move and exchange by diffusion in the immobile region. The values of the mobile-immobile partition coefficient, β , became smaller with increases in the pore water velocity (Tab.1). This was dependent on the initial tracer input in the presence of macropores, since a portion of the solute transported by preferential flow moves quickly down the soil column without fully interacting with the soil matrix. Increasing pore water velocity results in greater resistance to preferential flow through the macropores, so that convection and diffusion of ions in the mobile region will be reduced relative to the immobile region, resulting in reductions in the value of the mobile-immobile partition coefficient, β . In many studies, the mobile fraction has been assumed to be constant (Rao et al., 1980; Bajracharya and Barry 1997). However, experimental data from other studies showed that β tended to decrease with increasing pore water velocity when using curve-fitting procedures (Li et al., 1994a; Seyfried and Rao, 1987). This is consistent with the experimental results of this study.

Mass transfer coefficient, ω

The mass transfer coefficient, ω , characterizes the level of solute exchange between mobile and immobile regions. The mass transfer coefficient, ω , increased with increases in pore water velocity (Tab.1). DeSmedt (1979) and Wierenga (1996) found a linear relationship between the mass transfer area coefficient, ω_a , and the pore water velocity, v , in the mobile

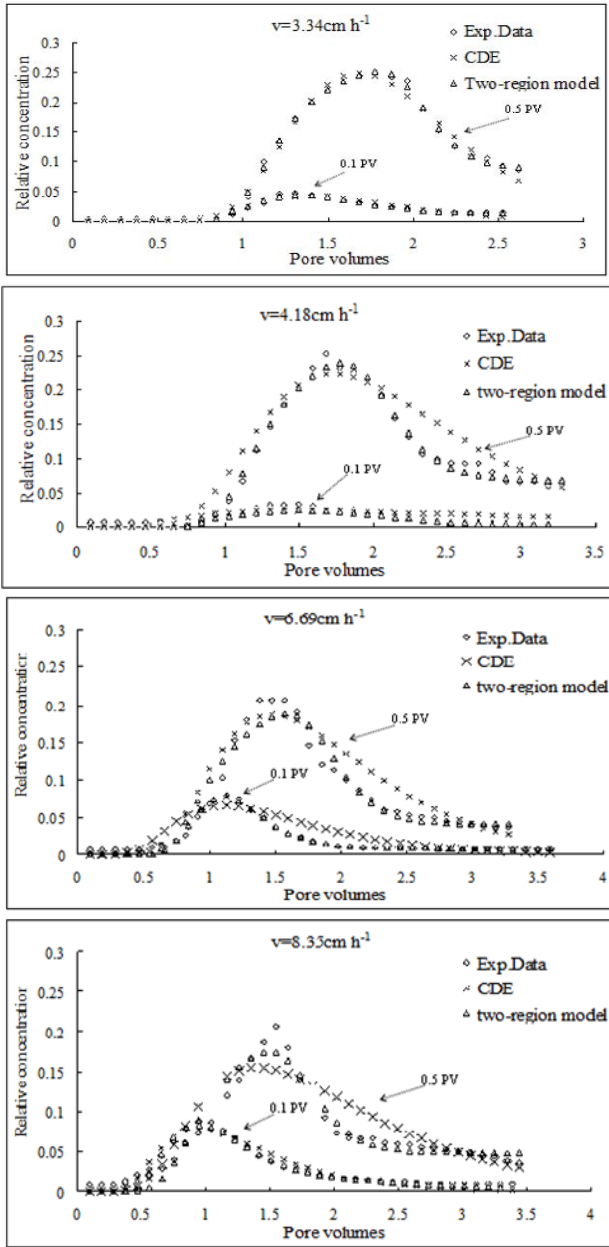


Fig 3. Influences of different input pulse volumes on breakthrough curves and the comparison between experimental data (Exp. Data) and the values fitted by the convection-dispersion equation (CDE) and two-region model

region given by: $\omega_a = 0.042v + 2.2$, which demonstrated that ω would also increase as the pore water velocity increased. That finding was consistent with the experimental results of this study. It also demonstrated that ω was not only dependent on the molecular diffusion coefficient but also on the distance and the cross-sectional area involved during diffusion.

Materials and methods

Model background and development

The earliest models based on chemical and physical non-equilibrium were the CDE and the two-region model (Skopp and Warrick, 1974; van Genuchten and Wierenga,

1976). During the last two decades, the focus has been on the two-region or the mobile-immobile concept. The most commonly used model in solute transport is the classical one-domain CDE (Lapidus and Amundson, 1952), which is characterized by a convection term with mean pore water velocity V (cm h^{-1}) and a hydrodynamic dispersion coefficient D ($\text{cm}^2 \text{h}^{-1}$):

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} \quad (1)$$

Where C is the solute concentration ($\mu\text{g ml}^{-1}$), t is the time (h), x is the spatial coordinate (cm), and R is the retardation factor. The following boundary and initial conditions are commonly applied for the CDE:

$$C = 0 \quad t = 0, \quad 0 < x < L \quad (2)$$

$$VC_0 = -D(\partial C/\partial x) + VC \quad x = 0, \quad 0 < t < t_p \quad (3)$$

$$0 = -D(\partial C/\partial x) + VC \quad x = 0, \quad t > t_p \quad (4)$$

$$\partial C/\partial x = 0 \quad x = L, \quad t > 0 \quad (5)$$

Where L is the solute transport length (cm); t_p is the duration of a solute pulse input (h); and C_0 is the solute concentration in the applied pulse ($\mu\text{g ml}^{-1}$). The two-region model (T-R), derived by van Genuchten and Wagenet (1989), is given by:

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D \frac{\partial^2 C_m}{\partial x^2} - v_m \theta_m \frac{\partial C_m}{\partial x} \quad (6)$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha(C_m - C_{im}) \quad (7)$$

$$\theta = \theta_m + \theta_{im} \quad (8)$$

Where θ is the volumetric water content ($\text{cm}^3 \text{cm}^{-3}$); θ_m and θ_{im} are the volumetric water contents in the immobile and mobile regions, respectively; C_m and C_{im} are the concentrations in the immobile and mobile regions ($\mu\text{g ml}^{-1}$); D is the diffusion coefficient ($\text{cm}^2 \text{h}^{-1}$); V_m is the mean pore water velocity in the mobile region (cm h^{-1}); t is the flow time (h); x is the spatial coordinate (cm); and ω is the mass transfer coefficient (h^{-1}). The general boundary conditions are given by:

$$C_i = 0; \quad 0 < x < l, t = 0 \quad (9)$$

$$V_i C_0 = -D_i \frac{\partial C_i}{\partial x} + V_i C_i; \quad (10)$$

$$0 = -D_i \frac{\partial C_i}{\partial x} + V_i C_i; \quad x = 0, t > t_p \quad (11)$$

$$\partial C_i / \partial x = 0; \quad x = l, t > 0 \quad (12)$$

The initial and boundary conditions of continuous input used in this study can be expressed as:

$$C = 0 \quad \text{or} \quad C_i = 0; \quad 0 < x < l, t = 0 \quad (13)$$

$$VC_0 = K \quad \text{or} \quad V_i C_0 = -D_i \frac{\partial C_i}{\partial x} + V_i C_i; \quad (14)$$

$$x = 0, t > 0$$

$$\frac{\partial C}{\partial x} = 0 \text{ or } \frac{\partial C_i}{\partial x} = 0; \quad x = l, t > 0 \quad (15)$$

Where D_i is the dispersion coefficient in the mobile region; V and V_i (C and C_i) are the pore water velocities in the soil and in the mobile region; l is the length of the experimental soil column (cm); and t is the input time of the solute (h). Using the derived values of the dispersion coefficients (D or D_i) from each of the fitted solute transport models, dispersivity, λ (cm) and the Peclet number, Pe , were calculated defined using the following equations (Peck and Watson, 1979):

$$\lambda = D / v \quad (16)$$

$$Pe = lv / D = l / \lambda \quad (17)$$

Column experiments

Four undisturbed soil columns (29.45cm diameter, 45cm long) were obtained from the A and B soil horizons (10-60 cm depth) at the Ansai field station, Shaanxi Province, on the Loess Plateau of China. Selected soil properties were: 0.60 kg kg⁻¹ silt content; 0.27 kg kg⁻¹ clay content; 0.005kg kg⁻¹ organic matter; 8.00 cmol kg⁻¹ cation exchange capacity; and 5.21 cmol kg⁻¹ Na exchange capacity. The particle size distribution was determined by sieving in combination with the pipette method; organic matter was determined by potassium dichromate titration; the cation exchange capacity was determined by BaCl₂ exchange; the percentage of exchangeable Na was determined by NH₄OAc exchange. Solute transport experiments were conducted to study the movement of a chloride tracer through the soil columns. In the laboratory, the bases of the columns were cut to give the desired soil column length (42cm). The outer walls were coated with a thin layer of paraffin wax and then each column was inserted into a steel cylinder. The upper surface of each soil column represented the actual field surface except that the litter and loose soil were removed in order to obtain a level surface. Chloride solute transport experiments were carried out using the miscible displacement method (Selim et al., 1987). Each soil column was saturated over a period of more than seven days by allowing a 0.005 mol L⁻¹ CaCl₂ solution, which helps to preserve the soil structure when compared to deionized water, to percolate through the soil from the soil surface. Several pore volumes of solution infiltrated the soil during this time. The water fluxes to be investigated (3.34 cm h⁻¹, 4.18 cm h⁻¹, 6.69 cm h⁻¹, 8.35 cm h⁻¹) were obtained by using a piston pump before the input of 0.15 mol L⁻¹ CaCl₂ solution pulses. Following the input of the solute, the effluent was collected in 500 ml volumetric flasks and then titrated with silver nitrate solution to determine the concentration of chloride ion (Cl⁻). Two types of chloride breakthrough curves (BTCs) were generated. The first type, referred to as a small pulse BTC, was generated by introducing a small pulse (0.1 pore volumes of 0.15 mol L⁻¹ CaCl₂) into each soil column; this small chloride pulse was recovered in four pore volumes of 0.005 mol L⁻¹ CaCl₂ solution after the small pulse application. The second type, referred to as a large pulse BTC, was generated in the same way as the first type except that the duration of the input pulse was longer (about 0.5 pore volumes). All the large pulse input experiments were carried out in the same columns as the small pulse input experiments, and immediately followed the small pulse experiments after ensuring the water flow was stable and the concentration of chloride in the effluent was

close to 0.005 mol L⁻¹.

Conclusions

In the experimental study of an undisturbed loessial soil, notable differences were found for the effect of different input pulses and pore water velocities on the process of solute transport. The effects were also reflected in the model parameters of the CDE and two-region model. Both models well-fitted the experimental data, although the two-region model generally had a higher prediction accuracy. An analysis of the model parameters showed that, when pore water velocity increased, the mobile-immobile partition coefficient tended to decrease and the mass transfer coefficient tended to increase. In order to accurately determine the changes and differences among the various model parameters under different conditions, they should be obtained from replacement experiments, whereby different conditions are applied to the same soil matrix. This form of research should be further advanced to better control conditions.

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