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Simulation of Chloride Transport Based Descriptive Soil Structure

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There is a need of environmental implications of rapid appearance of surface by applying chemical at depths below the vadose zone (tile line or shallow groundwater) for developing better insight into solute flow mechanism through the arable lands. Transport of chloride, a respresentative non-adsorbing solute, through a moderately structured silty clay loam soil (Gujranwala series, Typic Ustochrepts) and an un-structured sandy loam soil (Nabipur series, Typic Camborthid) was characterized and two existing models viz. convection dispersion equation (CDE) and preferential flow models were tested. The flux average of solute concentration in the outflow as a function of cumulative drainage was fitted to the models. The CDE fitted, relatively, better in the non-structured soil than in the moderately structured soil. Dispersivity value determined by CDE was very high for the structured soil which is physically not possible. The preferential flow model fitted well in the Gujranwala soil, but not in the Nabipur soil. The breakthrough characteristics i.e. drainage to peak concentration (Dp), symmetry coefficient (SC), skewness, and kurtosis were compared. Chloride breakthrough was earlier than expected based on piston flow. It indicated preferential flow in both the soils, yet, immediate appearance of the tracer in the Gujranwala soil demonstrated even larger magnitude of the preferential flow. Breakthrough curves' parameters indicated a large amount of the solute movement through the preferred pathways bypassing the soil matrix in the Gujranwala soil. The study suggests that some soil structure parameters (size/shape and degree of aggregation) should be incorporated in the solute transport models.

Key words**:** Soil structure, Solute transport, Simulation, Dispersitivity, Preferential flow.

Introduction

Loss of agricultural chemicals from agro-ecosystems and the subsequent groundwater contamination demand better understanding of water and solute movement in the root and vadose-zone. Simulation models are widely used for predicting water and solute movement through unsaturated soil (Steenhuis *et al* 1994; Hatfiel *et al* 1997). Discrepancies between model results and the actual field measurements often occur (Jury and Fluhter 1992; Steenhuis *et al* 1994). Many recent studies have depicted rapid increase in concentrations of surface when applied agro-chemicals in tile lines or shallow groundwater shortly after application (Mohanty *et al* 1998). In other studies, travel times of adsorbed and non-adsorbed chemicals have been found to be the same (Flury *et al* 1994; Camobreco *et al* 1996).

The classical convection-dispersion equation used for water and solute movement through the porous medium is valid as long as the porous medium is homogeneous and solute moves with a horizontally uniform wetting front (Khan and Jury 1990; Hatfield *et al* 1997). However, validity of this equation for field application has been challenged in the recent past due to soil textural and structural heterogeneity (Bouma 1991). Some pedological features viz. macropores, continuous inter-aggregated voids, earthworm burrows, decayed root channels and other geometric anomalies, have entirely different hydraulic properties than soil matrix and act as preferential flow pathways (Gupta *et al* 1999). The preferential pathways are small fractions of total porosity through which solutes travel rapidly, by passing the soil matrix (Radulovich *et al* 1992), causing a rapid and accelerated breakthrough (Buchter *et al* 1995; Gaber *et al* 1995).

Accurate estimation of water and solute velocities in soil profile is essential for the prediction of sub-soil and groundwater contamination. Solute transport can accurately be predicted once breakthrough curves over a range of flow rates have been established, which is cumbersome and impractical under field conditions. The soil structure description available in the soil survery reports can be correlated with the magnitude of preferentially-transported solutes and hence, possibly forms the basis to simulate models for agricultural chemicals loss. Objectives of the leaching study were to develop relationship between soil structure and magnitude of preferential flow and test applicability of the existing models for one-dimensional transport of non-adsorbing solute using $C1^-$ as tracer.

Models. Convection dispersion equation. The well-known convection-dispersion model assumes that dispersion process is formally equivalent to the diffusion. Even though the dispersion is a convective transport process and solute

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samples all pore spaces with an average velocity with dispersion around the front. The convection-dispersion equation for one-dimensional transport of adsorbing and non-adsorbing solutes in one or two domains has been solved for several boundary conditions (Parker and van Genuchten 1984; Marshall *et al* 1996). A constant adsorption partition coefficient is employed to solve the differential equation for adsorbing solutes and movement of solutes is scaled with a retardation coefficient, R. Thus, the average velocity is R times slower and time of arrival is R times longer compared to a non-adsorbing solute. In the one-domain model, the whole profile is assumed to take part in the transport of the solutes. In the two-domain model, the liquid phase is partitioned into mobile and immobile domains and the solute exchange between the two liquid regions is modeled as a first-order process (Parker and van Genuchten 1984).

Preferential flow model. The preferential flow model assumes that the flow through the macropores is fast and no interaction takes place with the soil matrix. This model is simple and requires minimum parameters to be fitted (Steenhuis *et al* 1994). It is assumed that the flow in the distribution layer can be described with the linear reservoir theory (Gelhar and Wilson 1974) and that no interaction with the soil matrix takes place below the distribution layer. The cumulative loss of solutes, L, in the preferentially moving water from a soil with a distribution layer of thickness D, can be written as (Steenhuis *et al* 2001).

$$L = Mo\,[1\text{-}exp\,(-\frac{Y}{W})] \qquad \textbf{(1)}$$

Where,

W = Apparent water content and equals $D(\rho\, k_d + \theta_s)$,

Y = The cumulative amount of percolation since the application of solute,

Mo = Initial amount of solute applied.

This equation is similar in form to that used by the U.S. Environment Protection Agency (1992) in predicting the loss of metals from the incorporation zone of sludge. The preferential flow model has been used to predict the loss of $C1^{-}$, pesticides, blue dye and metals when the matrix flow in the vadose zone could be neglected (Steenhuis *et al* 1994; Steenhuis *et al* 2001).

Materials and Methods

Site description. The soils were located at longitude 72.1°E and latitude 34.4°N in Potohar plateau (Pakistan) in sub-humid continental climate developed in Subrecent floodplain of Korang River (Khanzada 1976). Two soils-Nabipur, a sandy loam Typic Camborthid and Gujranwala (silty clay variant), silty clay Typic Ustochrepts were selected for the study. The Nabipur soil is deep, well drained, moderately calcareous and loam developed on level to nearly level position of the flood-plain. It has very friable, massive and sandy loam top-soil underlain by friable loam B horizon with weak, coarse and sub-angular blocky structure. The Gujranwala (silty clay variant) is very deep, well drained and non-calcareous and the soil is developed in nearly leveled parts of convex slopes. The soil has moderate and medium sub-angular blocky silty clay loam surface and moderate, coarse and medium, sub-angular blocky silty clay 'B' horizon. The Nabipur soil has been under rain-fed wheat-maize cropping with annual moldboard tillage operation while the Gujranwala soil remained untilled for the last 4 years.

Excavation and Preparation of soil columns. Six intact soil columns, three for each soil, were extracted by hand-excavating and carving leaving soil pedestals in the centre of the soil pit. The pedestals were carefully trimmed to closely fit in the 260 mm diameter and 390 mm long PVC pipes. The space (≈ 10 mm) between the PVC pipe and the pedestals was filled with melted paraffin wax. The columns were transported to the laboratory. Undisturbed soil cores were also taken from 30 to 80 mm, 130 to 180 mm and 230 to 280 mm depths to determine the soil bulk density. Total porosity was calculated, assuming particle density 2.65Mg/m^3. Bottom and top of the columns were trimmed and smoothed in the laboratory. Further, 5 to 7 mm of bottom soil was removed and 0.05 to 0.02 mm fine sand was filled and covered by the nylon gauze sheet to ensure good hydraulic contact between the column and collection chamber. Finally, a perforated aluminum sheet was fixed at the bottom to firmly support the sand and the nylon gauze sheet. The sand had 3.4 mm/s saturated hydraulic conductivity and 1.52 Mg/m^3 bulk density. The nylon gauze sheet and aluminum sheet had 81 mesh openings. The column rested on a collection chamber, sealed with silicon rubber sealant. Polythene drain tube was fixed to both the holes. The collection chamber had attached two drinage tubes, one was used to drain leachate to sampling bottle and the other served as a peizometer. Each column had two microtensiometers fixed at 70 and 220 mm below the soil surface to ensure constant saturation.

Each column was slowly saturated from the bottom through the drain tube attached to the chamber. Saturation was achieved in 4 days by raising the water reservoir 100 mm in a day until water appeared at the surface. Water was kept ponding for further 48 h to ensure complete saturation. During saturation one drain tube attached to the chamber in order to bleed air. To maintain the constant ponding on the surface of the column, a water supply reservoir (Mariotte siphon) with

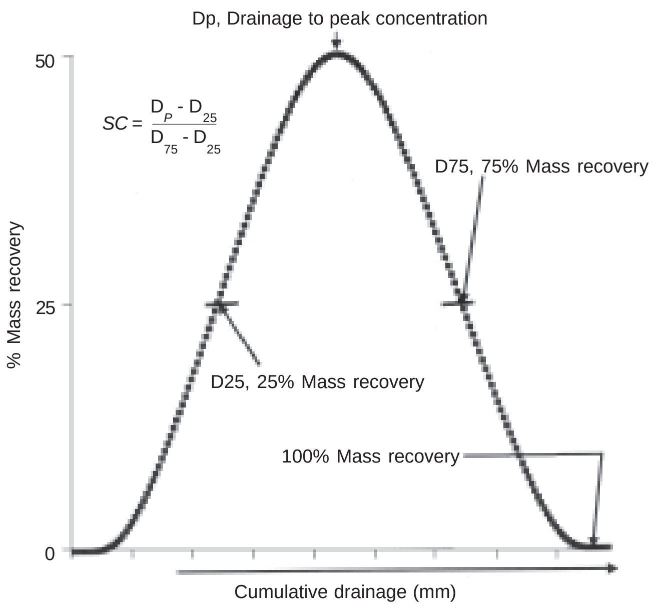

Fig 1. A hypothetical symmetrical distribution indicating symmetry coefficient as 1.

adjustable elevation was conected directly to the surface of the column. Saturated hydraulic conductivity (Ks) was measured with a constant head method by maintaining water level 30 mm above the column surface. Mean flow velocity (V) was calculated from Ks, assuming that water flux passed through all the water-filled pores.

Leaching experiment. Saturated columns were flushed with two-pore volume of 15 mM $LiNO_3$ solution at 30 mm head to displace interstitial anions with NO_3. Application of $LiNO_3$ solution ended at steady state condition with inflow equal to the outflow. Then the columns were leached with 15 mM Cl^- using LiC1 solution. When effluent $C1^-$concentration reached approximately 15 mM, the application of LiC1 solution stopped and the $LiNO_3$ solution started again to displace $C1^-$. Finally, $LiNO_3$ leaching stopped when effluent $C1^-$ concentration dropped below 0.02 mM. The effluent $C1^-$ concentration and effluent volumes were recorded. Chloride concentration was determined using the Fisher Accumet 950 pH/Ion meter using $C1^-$ specific electrode.

Parameter estimation. The breakthourgh curves (BTCs) depicted relative concentration (C/Co) versus percolate depth (drainage volume per unit surface area). Solute flow parameters were calculated from the breakthrough data by using convection-dispersion and the preferential flow models. Other indicators of preferential flow included symmetry coefficient (SC), percolate depth to peak concentration (Dp), and skewness and kurtosis of the curves (discussed later).

The CDE was executed using CXTFIT (Toride *et al* 1995). By assuming one domain vertical transport of Cl^- without adsorption solute velocity (V) and dispersion (D) were obtained. The simple preferential flow model (equation 2) (Steenhuis *et al* 1994; Steenhuis *et al* 2001) yielded apparent water content (W), in which depth of water was required to leach 50% of mass applied.

$$1n\,(1-\frac{L}{M_o}) = \frac{1}{W}\,Y \text{ .... } \mathbf{(2)}$$

In $(1-L/M_o)$ was plotted against drainage (Y), where L was successive cumulative solute mass loss corresponding to respective cumulative drainage depth. Using a linear regression with Y as the dependent variable and 1n(1-L/Mo) as the independent variable without intercept, W was the inverse of the slope. In both the models r^2 depicted goodness of fit.

Symmetry coefficient (SC) of curve proposed by Hatfield *et al* (1997) was modified by replacing time with cumulative drainage (Fig 1). It was a ratio of the two differences: (a) the difference between drainage to peak concentration and 25% mass loss and (b) the difference between drainage to 75% mass loss and to peak concentration. Skewness and kurtosis of the curves were calculated by using PROC NPARIWAY (SAS Inc 1996).

Table 1
Physical properties of soil columns

Soil	Column	Bulk density (Mg/m^3)	Total porosity (m^3/m^3)	Ks† (mm/day)	Velocity (mm/day)	Macropores Surface	Macropores Bottom
Nabipur	1	1.57	0.41	17.50	42.90	1	2
	2	1.54	0.42	29.90	71.20	2	1
	3	1.58	0.40	16.40	41.00	0	4
Gujranwala	1	1.48	0.44	28.10	63.90	0	6
	2	1.45	0.45	31.90	70.90	1	7
	3	1.51	0.43	27.20	63.30	3	5

† Saturated hydraulic conductivity.

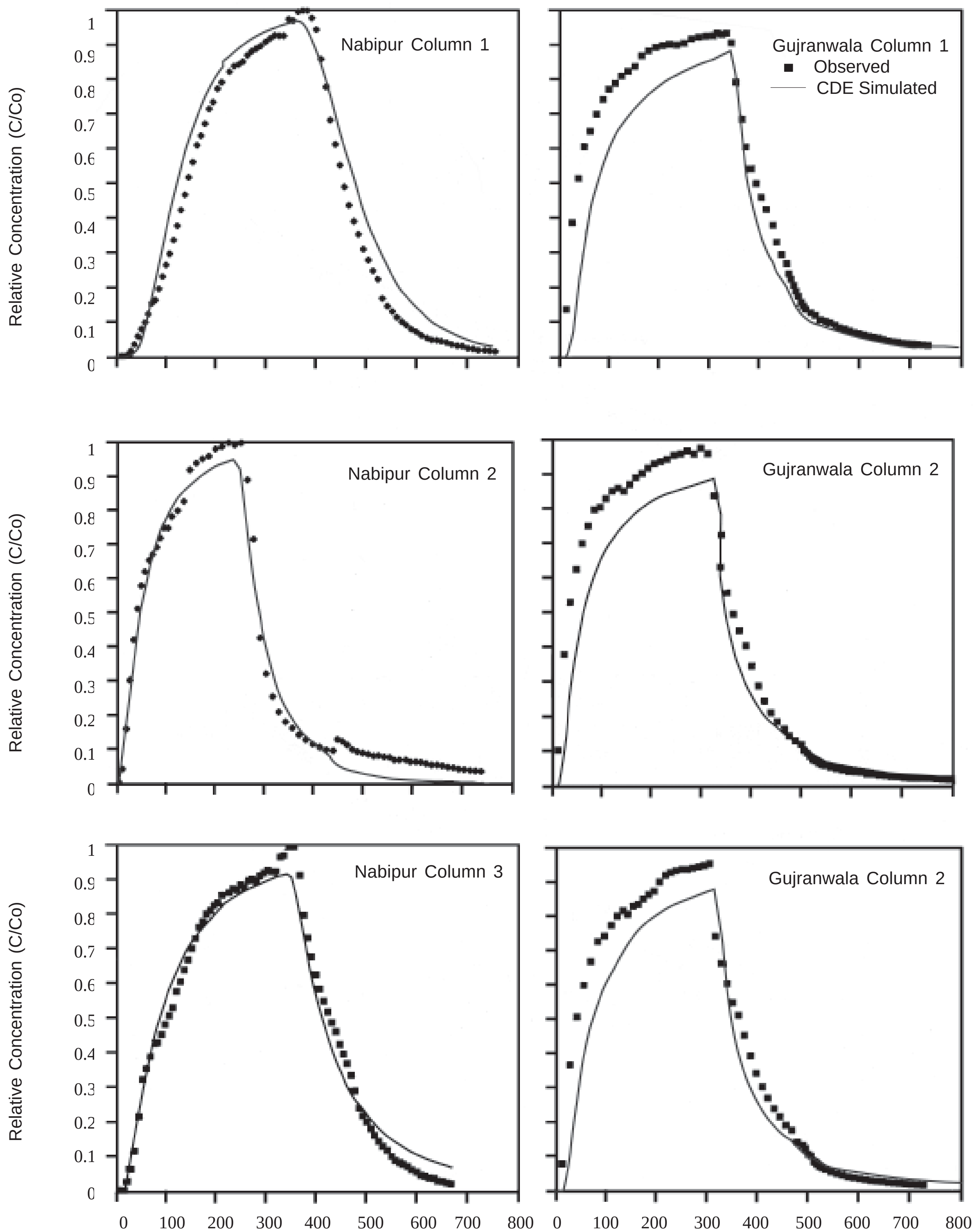

Fig 2. Chloride breakthrough in the Nabipur and Gujranwala soil columns.

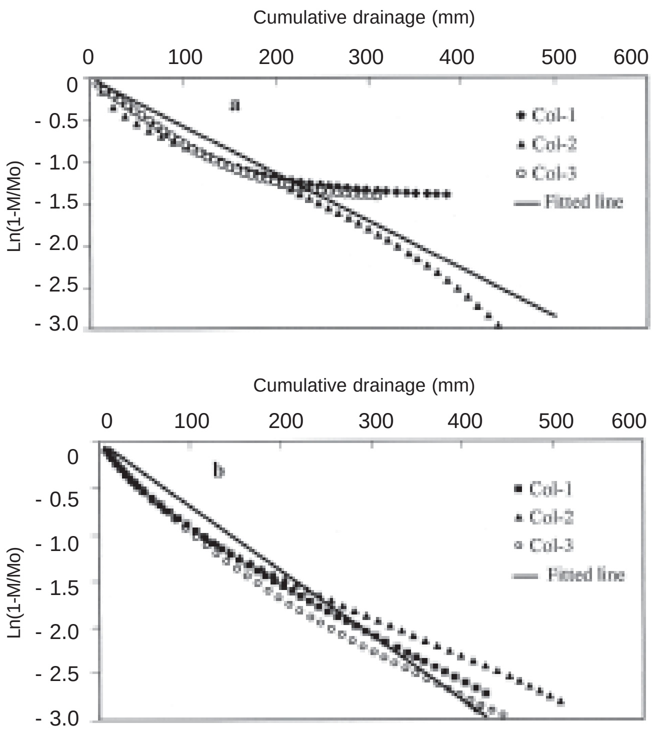

Fig 3. Preferential Flow Model (In (1M/Mo) vs cumulative outflow) fitted in (a) Nabipur and (b) Gujranwala soil columns.

Table 2
Characteristics of breakthrough curves

Soil	Column	Dp† (mm)	Tp‡ (h)	SC§	Skewness	Kurtosis
Nabipur	1	370	24.00	5.70	0.29	1.56
	2	250	10.50	10.80	0.77	1.09
	3	340	22.00	7.00	0.01	1.51
Gujranwala	1	300	13.00	16.90	0.56	1.41
	2	250	12.00	10.10	0.67	1.31
	3	290	13.00	15.10	0.59	1.38

† Drainage to peak concentration; ‡ Time to peak concentration; § Symmetry coefficient.

Results and Discussion

Soil physical characteristics. Columns extracted from Nabipur soil had greater bulk density than those extracted from Gujranwala soil (Table 1). The Nabipur soil, was sandy loam and weakly structured, with an average bulk density of 1.51, 1.61, and 1.56 Mg/m^3 in the Ap, Bwt, and Bt horizons, respectively. The corresponding horizons in the moderately structured silty clay soil (Gujranwala) had a bulk density of 1.48, 1.49, and 1.51 Mg/m^3. A relatively greater bulk density of Bw horizon of the Nabipur soil than that of the Gujranwala soil was noticeable and can be ascribed to mechanical compaction of the sandy loam material. However, column bulk density, on the whole, was very close to the calculated average of the profile. The column 2 of Nabipur soil had lower bulk density than the column 1 and 3. It is interesting to note that the Gujranwala soil contained a greater number of visible macropores than the Nabipur soil. Consequently, the greater porosity and probably pore continuity in the Gujranwala soil columns resulted in larger hydraulic conductivity than the Nabipur columns.

Chloride breakthrough. In both the soils, $C1^-$ breakthrough occurred earlier than one pore volume (Fig 2). In all the Gujranwala soil columns, $C1^-$ breakthrough was almost immediate. Initially, slope of the breakthrough curve was steep and relative concentration (C/Co) reached 0.5 only after 40 mm of cumulative drainage. Afterwards, the slope of the curve declined relative to the initial slope and C/Co reached to 0.75 with another 40 mm cumulative drainage. The peak C/Co (0.95) in the Gujranwala soil columns was obtained with 300 mm cumulative drainage. During the flushing phase, when chloride application had stopped and $C1^-$ free water had started leaching, there was an immediate and sharp decline in percolate Cl^-. In contrast, the $C1^-$ breakthrough in the Nabipur soil columns was delayed by approximately 25 mm, and the concentration ratio of 0.5 was attained after 125 mm percolate depth and 0.75 with 200 mm. The peak C/Co of 0.95 was obtained after 350 mm cumulative drainage. Moreover, the concentration ratio decreased gradually in this soil after termination of $C1^-$ application and there was less tailing in the Nabipur soil as compared to that of the Gujranwala soil.

Curve shape parameters. The drainage to peak concentration (Dp), symmetry coefficient (SC) and skewness of $C1^-$ BTCs provided good comparison between the Nabipur and the Gujranwala soils (Table 2). A peak $C1^-$ concentration was achieved with lesser drainage in the Gujranwala soil columns compared to the Nabipur. Except for the column 2, drainage to peak concentration in Nabipur soil columns was 50 to 75 mm

Table 3

Summary of CDE† and preferential flow model results

Soil	Columns	Convection-Dispersion equation				Preferential flow model	
		D (cm^2/h)	V (cm^2/h)	λ (cm)	r^2	W (cm)	r^2
Nabipur	1	14.50	3.21	4.52	0.96	20.96	0.64
	2	172.20	9.89	17.41	0.98	15.11	0.94
	3	64.80	4.05	16.00	0.98	17.48	0.83
Gujranwala	1	255.40	6.94	36.80	0.97	14.37	0.96
	2	230.10	8.53	26.98	0.98	16.58	0.93
	3	156.20	7.33	21.31	0.96	13.81	0.95

† Convection-Dispersion equation.

which was greater than that of Gujranwala columns. Breakthrough curves from the Nabipur soil columns were relatively symmetrical and were less skewed as compared to the Gujranwala soil columns. The symmetry coefficient value in the Nabipur soil column curves was half that of the Gujranwala columns. Mean kurtosis values for both the soils were similar but the Nabipur soil took twice the time (1400 min) to achieve the crest as compared to the Gujranwala (740 min). The Nabipur soil column 2 behaved differently than the other two columns from the same soil.

The solute breakthrough occurred immediately in the structured (Gujranwala) soil and after 25 mm of drainage in the unstructured (Nabipur) soil (Fig 2). Further, in un-structured soil, the percolate amount was less than 0.3 pore volume whereas, under uniform flow exactly one pore volume of incoming solute would have been required to replace the pre-existing solute and breakthrough at outflow end by assuming zero dispersion (van Genuchten 1981). In a homogeneous cylindrical soil column, solute mixed completely in radial direction before it reached to the outflow end in the vertical direction. Therefore, the early breakthrough of the solute indicated the occurrence of preferential flow through all the columns of both the soils although the magnitude was greater in the structured than in the un-structured soil.

Preferential flow was caused by wetting front instability (DeRooij and DeVaries 1996), funnel flow in layered soils (Kung 1990) and flow through macropore by-passing the soil matrix (Sollins and Radulovich 1988; Gupta *et al* 1999). Macro-pores flow, through non-capillary inter-pedal void spaces, was associated with pedological cracks, decayed root channels and other structural anomalies essentially present in intact soil columns (Sollins and Radulovich 1988). The immediate breakthrough in case of the Gujranwala soil could be due to preferential flow through inter-ped void spaces or macropores. These results corroborated with the structural conditions of the soils as macropores resulted in greater inter-aggregate infiltrability than intra-aggregate infiltrability (Gupta *et al* 1999).

Model fitting. Convection dispersion and preferential flow models have been compared. The Convection-Dispersion equation used one-dimensional mode by assuming zero retardation (R) as $C1^-$ is non-adsorbing. The model parameters mean i.e. pore velocity (V), apparent dispersion coefficient (D) and r^2 (indicates the fitness of the model) were determined by using CXTFIT computer program (Toride *et al* 1995). Dispersivity (λ), solute dispersion to mass transfer per unit time or drainage outflow in a unit cross-sectional porous area, is D/V (Jury *et al* 1991). Except for one column, mean pore velocity of the un-structured soil was approximately two times un-structured soil (Table 3), indicating larger flow through non-capillary porosity. Dispersion in the structured soil columns was larger than the un-structured soil but was highly variable. Surprisingly, in all the three Gujranwala soil columns best-fit solution ($r^2 > 0.96$) was achieved at $D > 150$ cm^2/h. This large D value implied no mass transfer of water had occurred and the movement of $C1^-$ was solely due to diffusion. This resulted in extremely high dispersivity values (21 - 37 cm) that were physically impossible. Dispersivity ranged from 4.5 to 17.4 cm for the non-structured soil, which were within acceptable limits (Jury *et al* 1991). Therefore, although the CDE model simulated the general shapes of the BTC, except the initial breakthrough and the peak, it predicted an erroneous dispersivity in the structured soil.

In contrast, the preferential flow model was better fit in the structured soil than in the un-structured soil as indicated by a fairly straight line in the later case (Fig 3). If the preferential flow model is valid then the data should plot reasonably well as a straight line. The regression results showed that the data fit the preferential flow model very well (Table 3). The r^2 for the three columns from the Gujranwala soil was 0.93 or higher and with an exception, it was 0.83 or less for the Nabipur soil. One column in Nabipur soil did fit to a straight line, which reflects either an artifact or natural variability.

In the Gujranwala soil, the conductivity of the matrix was relatively low than in the Nabipur soil. Thus, no exchange of solutes took place between macropores and matrix for the Gujranwala soil which was assumed in the preferential flow model (Steenhuis *et al* 1994). This is not true for the Nabipur soil, showing a deviation from the straight line probably because of increasing concentration (Steenhuis *et al* 2001). The theory assumes that the mixing is instantaneous and that there is no delay in travelling time from the distribution zone to the bottom of the column. In this study, we plotted part of the data set (natural log of mass of Cl^- remaining vs. the cumulative outflow) starting immediately after the effluent Cl^- had reached maxima as mixing was not instantaneous in this case. Therefore, the initial deviation from straight line is not depicted in the graph.

Curve shape parameters. The curve parameters i.e. drainage to peak concentration (Dp), symmetry coefficient (SC) and skewness provided comparison between the Nabipur and Gujranwala soil columns (Table 2). Compared to the Nabipur soil, the peak Cl^- concentration in the Gujranwala soil columns was attained with less drainage due to inter-void spaces conducting greater solute compared to matrix. This phenomenon is related to differences in soil structure. However, time to peak concentration had greater magnitude of difference between the two soils compared with drainage to peak concentration because higher flow rate in the structured soil also allowed more water to drain in given time. As such the Nabipur soil columns required twice the time to attain the peak Cl^- concentration than the Gujranwala soil while the difference in drainage was not so high.

The peak concentration would coincide with loss of 50% mass in a symmetrical bell-shaped curve. A symmetry coefficient close to one indicated the symmetricl distribution and value >1 indicate preferential flow. The Gujranwala soil had about two times larger SC than the Nabipur soil. The faster translocation of mass in the Gujranwala soil compared with the Nabipur soil was obvious as the peak concentration in the Gujranwala soil columns coincided with about 75% of the total mass loss, which was about 60% in the Nabipur soil. Kurtosis values of BTCs, another quantitative indicator of preferential flow (Hatfield *et al* 1997), were slightly higher in the Nabipur soil than in the Gujranwala soil. The reported results are contrarily to Hatfield *et al* (1997) to the extent that kurtosis is a better numeric indicator of preferential flow than skewness and SC, whereas we found DP, skewness, and SC better numeric indicators than kurtosis.

Conclusion

Comparison of calculated and observed first arrival times and BTCs indicated that perferential flow occurred in all the columns from both the soils. However, the magnitude of preferential flow was higher in the Gujranwala soil than in the Nabipur soil. Drainage to peak concentration, symmetry coefficient, and skewness of the BTC were quantitative parameters for perferential flow and their statistical comprison has potential for field application. Further, the CDE described well the solute transport through the un-structured soil but failed in case of the structured soil while the reverse was true for the preferential flow model. The study indicates a need for incorporation of soil structure parameters (size/shape and degree of aggregation) in the solute transport models in order to improve simulation.

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