

Water and solute movement in soil as influenced by macropore characteristics

1. Macropore continuity

S.E. Allaire-Leung ^{a,*}, S.C. Gupta ^b, J.F. Moncrief ^b

^a *US Salinity Laboratory, 450 W. Big Springs Road, Riverside, CA 92507, USA*

^b *Department of Soil, Water, and Climate, University of Minnesota, St. Paul, MN 55108, USA*

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Abstract

In most contaminant transport modeling studies, only the macropores that are visible at the soil surface are considered. Furthermore, it is assumed that these macropores are straight and continuous throughout the soil profile. Little is known on the importance of other types of macropore continuity and tortuosity on preferential movement of contaminants through soils. This paper describes the results of a laboratory study dealing with macropore continuity effects on breakthrough curves (BTCs) and solute distribution in a Forman loam (fine-loamy mixed Udic Haploborolls) soil. BTCs were obtained under a constant hydraulic head of 0.08 m from a 2-D column (slab) containing artificial macropores. The input solution contained 1190 mg l⁻¹ KBr, 10 mg l⁻¹ Rhodamine WT, and 100 mg l⁻¹ FD&C Blue #1. The continuity types studied were: macropore open at the soil surface–open at the bottom of the column (O–O), open–closed (O–C), closed–open (C–O), and closed–closed (C–C). A treatment without macropore served as a control. As expected, the solution in the O–O treatment reached the bottom of the macropore about 100 times faster by bypassing most of the soil matrices. As a result, the breakthrough time for O–O treatments was much faster than any other continuity treatments. Both the O–O and O–C type macropores favored earlier breakthrough, smaller apparent retardation coefficient (R'), deeper center of mass, and higher anisotropy in tracer concentrations in the horizontal direction than the C–O, C–C, and the Control treatment. The C–C macropore was favored in deeper penetration of tracer only when another macropore was present nearby. The importance of macropore continuity increased with an increase in the adsorption coefficient of the tracers. © 2000 Elsevier Science B.V. All rights reserved.

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* Corresponding author. E-mail: sleung@ussl.ars.usda.gov

1. Introduction

Several studies have been undertaken to understand the factors that control preferential flow through soil (Gish and Shirmohammad, 1991). Most of these studies have been conducted on undisturbed soil columns where macropore morphology is usually unknown. Often, breakthrough curves (BTCs) are the only measurements taken to characterize the presence or absence of macropores (Pearson et al., 1996; Ashraf et al., 1997). In a few cases (Ogden et al., 1992), simple parameters such as macroporosity or average macropore length have been used to describe the macropore population.

It is well-understood that the conventional approach of using simple parameters to describe macropores is not sufficient to predict preferential transport of water and solute in soils. Munyankusi et al. (1994) concluded that the number and size of visible surface macropores were not sufficient to model water and solute transport through macroporous soils. These authors observed that besides the number and size of macropores, one also needs the length and the continuity of macropores.

Even in studies where macropores have been characterized in detail using computed tomography scan (Cook, 1996) or paint injection technique (Munyankusi et al., 1994), it has been difficult to isolate the impact of macropore characteristics such as continuity and tortuosity on preferential flow. A few experiments that have been conducted with artificial macropores in repacked soil columns have often used macropores open at the surface and parallel to the direction of the flow (Steenhuis et al., 1994). It is unknown how other types of macropore continuity or tortuosity impact preferential transport. Furthermore, most studies that have assessed the impact of macropores on preferential flow have used a conservative tracer in breakthrough characterization (Gish and Shirmohammad, 1991). An important characteristic of the contaminants is their adsorption–desorption characteristic. This characteristic varies with soil type, soil wetness condition, and the type of contaminant. It is unclear how macropore continuity or tortuosity interacts with contaminants of different adsorption characteristics to affect preferential transport.

The goal of this research was to quantify the impact of various macropore continuity and tortuosity levels on preferential transport of conservative and adsorbed chemicals in artificially packed 2-D soil columns (slabs). This paper discusses (1) the effect of macropore continuity on BTCs, apparent retardation coefficients, and concentration distribution profiles of both conservative and adsorbed tracers, and (2) how the proximity of other macropores alters the relative importance of macropore continuity on preferential transport. A companion paper (Allaire-Leung et al., 2000) presents the effects of macropore tortuosity on solute transport.

2. Materials and methods

2.1. Soil and tracers characteristics

The soil used in this study was the B horizon of a Forman loam (sand = 40%, silt = 35%, clay = 25%, pH with 1:2 CaCl₂ = 7.6). The soil has been air-dried, ground

and sieved through a 2-mm sieve. The saturated soil hydraulic conductivity, saturated water content, and residual water content were $4.7 \times 10^{-7} \text{ m s}^{-1}$, $0.53 \text{ m}^3 \text{ m}^{-3}$, and $0.23 \text{ m}^3 \text{ m}^{-3}$, respectively. The soil was collected from a site at the University of Minnesota Agricultural Experimental station in Morris, MN.

The three tracers used in this study were: bromide, FD & C Blue #1 ($\text{C}_{37}\text{H}_{34}\text{N}_2\text{Na}_2\text{O}_9\text{S}_3$) and Rhodamine WT ($\text{C}_{19}\text{H}_{29}\text{N}_2\text{O}_5\text{Na}_2\text{Cl}$). The reasons for selecting these tracers were that: (1) they cover a wide range of adsorption characteristics; (2) their background levels in the soil are very low (Trudgill, 1987; Everts et al., 1989); (3) they have low toxicity (Smart, 1984; Flury and Papritz, 1993; Flury and Flüßler, 1994); (4) the potential for their decay is small (Smart and Laidlaw, 1977); (5) they have high water solubility (Smart and Laidlaw, 1977); and (6) they are relatively easy to measure (Davis et al., 1985).

Bromide, a non-adsorbing tracer, was applied as KBr. The FD&C Blue #1 has a molecular weight of 783 and is highly adsorbed on soil particles (Flury and Flüßler, 1995). The Warner–Jenkinson¹ lists the dye as 89% pure with water, salt, and impurities making up the rest. The FD&C Blue #1 dye concentrations reported here are in terms of dye as is, i.e., without corrections for impurities. The FD&C Blue #1 is non-fluorescent and has $\text{p}K_a$ of 5.8 and 6.6, i.e., two of its functional groups act as anions above these pH values. Additional characteristics of the FD&C Blue #1 dye are given in Flury and Flüßler (1995) and Perillo et al. (1998).

Rhodamine WT was bought as Keyacid Rhodamine WT liquid (Keystone Aniline¹, Chicago, IL) and was 19.3% pure (Cook, 1996). The concentrations reported here are in terms of pure Rhodamine WT, i.e., corrected for impurities. Rhodamine WT has a molecular weight of 566, and is considered as an anion in soil solution due to dissociation of Na^+ (Smart and Laidlaw, 1977). Its adsorption characteristics appear to be in between the adsorption characteristics of KBr and FD&C Blue #1 (Sabatini and Austin, 1991). Rhodamine WT is fluorescent and has a $\text{p}K_a$ of 1.3 (Smart and Laidlaw, 1977).

2.2. Approaches

In this study, two experiments were conducted. The first experiment tested the influence of macropore continuity on water and solute movement with a single macropore per column. The second experiment investigated the importance of macropore continuity with three macropores per column.

For the first experiment, a rectangular plate chamber made of plexiglass with inside dimensions of 0.3 m wide, 0.70 m high, and an average thickness of 0.01 m was used to construct soil columns with artificial macropores (Fig. 1). The chamber had five equally spaced outlets at the lower boundary for leachate sampling. The outlets were made of cylindrical plexiglass tube with 9 mm inner diameter. In this experiment, only one macropore was positioned in each column. The macropores were constructed from stainless steel screen (50 holes cm^{-2}). They were straight with a square cross-section

¹ The names are provided for the readers and are not an endorsement from the University of Minnesota.

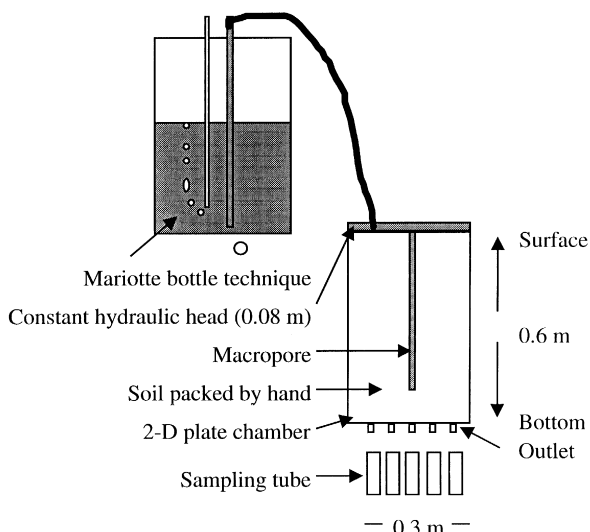


Fig. 1. Schematic representation of the experimental set-up.

and were $0.01 \times 0.01 \text{ m}^2$ wide, and 0.45 m long, except that the O–O macropore was 0.60 m. The macropores were positioned in the plate chamber. The soil was then packed around them by hand to a height of 0.60 m with an average bulk density of 1.55 mg m^{-3} and a standard deviation of 0.08 mg m^{-3} . A thin layer of sand (average particle size of 0.625 mm) was placed at the soil surface to prevent soil disturbance during solution application.

The breakthrough experiments simulated water and solute movement into an initially dry soil under ponded conditions. During the experiment, a constant hydraulic head of 0.08 m was maintained at the upper boundary with a Mariotte bottle setup (Fig. 1). The lower boundary condition for the BTC experiment was free drainage. The input solution contained 1190 mg l^{-1} of potassium bromide, 10 mg l^{-1} of Rhodamine WT, and 100 mg l^{-1} of FD&C Blue #1. After the addition of 1.5 pore volume (PV) of this solution, the input solution was switched to a solution that contained only 10 mg l^{-1} of Rhodamine WT and 100 mg l^{-1} of FD&C Blue #1. The surface of the plate chamber was kept covered with a plastic sheet to minimize evaporation of the applied solution.

In this paper, the term ‘continuity’ refers to whether the macropores are open or closed at the boundaries of the soil column. Four types of continuity were studied (Fig. 2): macropore open at the soil surface and open at the lower boundary (O–O), open at the surface and closed at the lower boundary (O–C), closed at the surface and open at the lower boundary (C–O), and closed at both ends (C–C). The Control treatment did not contain macropore.

The set-up for the second experiment was similar to that of the first experiment, except that the column chamber was 1.00 m wide and 0.40 m high (Fig. 3). The soil was packed to a height of 0.3 m. The Mixed treatment consisted of a mixture of macropores of various characteristics. The combination of macropore types included in this set-up

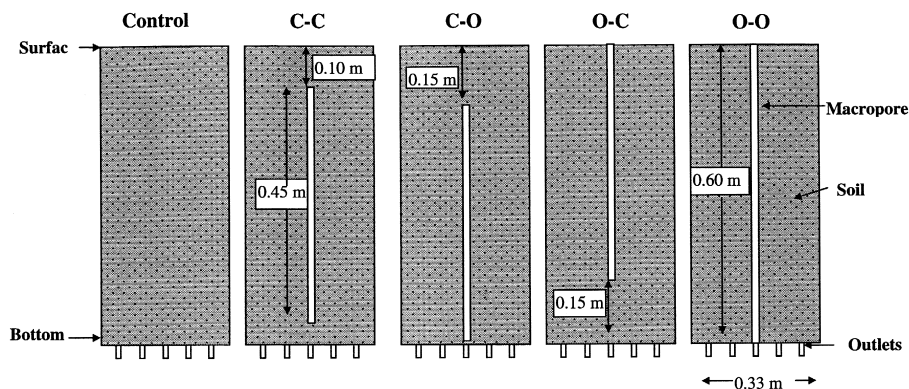


Fig. 2. Position of the macropore in soil columns of different continuity treatments (not scaled).

was: O–C vertical, O–C inclined, and C–C inclined (Fig. 3). The Control treatment in this experiment had three equally spaced straight O–C vertical macropores. All macropores were 0.20 m long. The BTCs were run under a constant hydraulic head of 0.05 m.

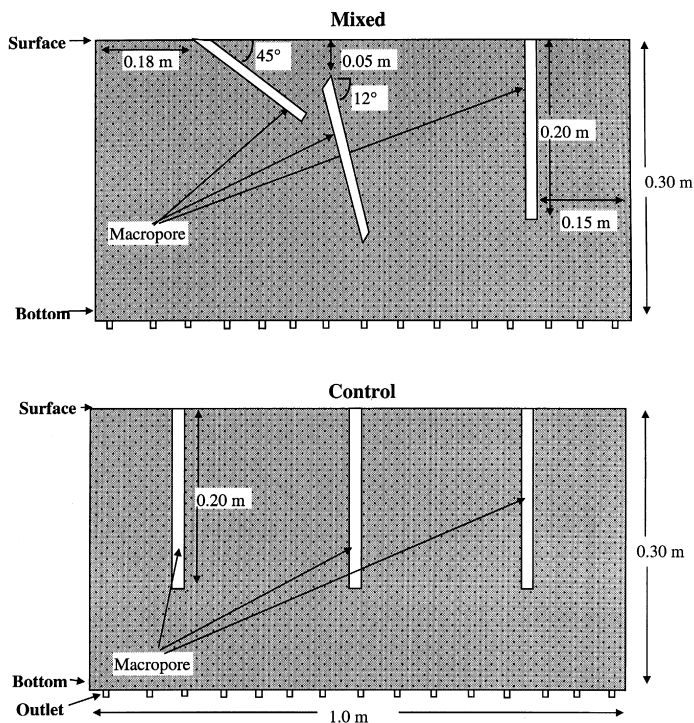


Fig. 3. Position of the macropore in soil columns for two different macropore populations (not scaled).

Average bulk density of the soil columns was 1.55 mg m^{-3} with a standard deviation of 0.11 mg m^{-3} .

All the leachates were sampled from each of the five outlets for the first experiment and 15 outlets for the second experiment at the lower boundary of the soil column using a 50-ml polypropylene centrifuge tubes. Leachate samples were taken several times during the first 2 days and subsequently once or twice a day, depending upon the velocity of the percolating solution for a total of about 40 samples. The breakthrough experiments were stopped when 8 and 10 PV of applied solution had passed through the soil columns in Experiments 1 and 2, respectively. The PV in each treatment and replicate has been calculated from the soil bulk density considering macropore as empty spaces. A PV in this paper refers to volume of solution applied at the soil surface.

In this paper, breakthrough time refers to a number of PVs (relative time) taken by a tracer to appear at a detectable level ($0.01 \text{ C}/\text{C}_0$) at the bottom of the column. The retardation factor (R) was calculated either from the length or the time measurements.

Length measurements:

$$R = \frac{V_{\text{H}_2\text{O}}}{V_{\text{tracer}}} = \frac{L_{\text{H}_2\text{O}}}{t} \frac{t}{L_{\text{tracer}}} = \frac{L_{\text{H}_2\text{O}}}{L_{\text{tracer}}}, \quad (1)$$

Time measurements:

$$R = \frac{L}{t_{\text{H}_2\text{O}}} \frac{t_{\text{tracer}}}{L} = \frac{t_{\text{tracer}}}{t_{\text{H}_2\text{O}}}, \quad (2)$$

where $V_{\text{H}_2\text{O}}$ and V_{tracer} are the velocity (m s^{-1}) of water and tracer fronts, respectively; $L_{\text{H}_2\text{O}}$ and L_{tracer} are distance (m) to the water and tracer fronts, respectively; $t_{\text{H}_2\text{O}}$ and t_{tracer} are the time (s) to breakthrough for water and tracer, respectively; and L is the length of the soil column (m). Since measurement of time and distance to dye fronts includes the effect of both the soil matrix and the macropores, we define this retardation as an apparent retardation factor (R'). This is different from the retardation coefficient factor (R) solely due to soil matrix as in the Control treatment. R' was calculated at different times since we expected it to change with time as a result of a decrease in water flow and due to an interaction between FD&C Blue #1 and KBr (Allaire-Leung et al., 1999). The apparent retardation coefficient of FD&C Blue #1 at a given time was calculated using the depth of the dye front relative to the wetting front (Eq. (1)). The depth was the deepest depth observed at a given time. R' of Rhodamine WT could not be estimated using the depth technique because the color contrast with the soil was too small. Therefore, the apparent retardation coefficient of Rhodamine WT was calculated using the times it took for the water and the dye to reach any of the five outlets at the bottom of the column (Eq. (2)). This technique could not be used for the FD&C Blue #1 because, in some treatments, it took too long for the dye to reach the lower end of the column (many days). We believe that each technique may lead to a different estimate of R' , but a comparison of the retardation value from three replications using the same technique gave very consistent results. Furthermore, these numbers were comparable to retardation values obtained from other laboratory results (Allaire-Leung et al., 1999).

After the completion of BTCs, the soil columns were taken apart and sampled to evaluate the concentration distribution of Rhodamine WT and FD&C Blue #1. In Experiment 1, 50 samples of 2.5 g each were taken from the side wall to the side wall of the column (wall-trimmed). The visual distribution of FD&C Blue #1 dye was used as a sampling guide. Samples were taken at higher frequency in regions where FD&C Blue #1 concentration varied faster with distance. They were equally spaced in the horizontal direction. Therefore, the sampling grid varied from treatment to treatment and replicate to replicate. In Experiment 2, we took 100 samples from each of the soil columns. This higher number of samples was chosen because the columns in the second experiment were larger and contained three macropores.

For the extraction of tracers, the samples were shaken with 25 ml of de-ionized water (1:10 ratio) on a reciprocating shaker (Model R2, Fisher Scientific¹, New Brunswick, Edison, NJ) for 24 h at 200 rpm. After shaking, the samples were centrifuged (Fisher Scientific 26KM Centrifuge Marathon¹, Pittsburgh, PA) at 6000 rpm for 20 min. The supernatant was then transferred to clean tubes and the tracer concentration was measured as described below.

Bromide concentration in solution was measured using a specific bromide electrode (Orion 9435, Orion Research¹, The Schrafft Center, Boston, MA). The FD&C Blue #1 concentration in solution was determined by measuring the absorbance of the solution sample at 630 nm using UV/Visible spectrophotometer (Milton Roy Spectronic 401¹, Rochester, NY). Rhodamine WT was measured using a luminescence spectrometer (Perkin-Elmer LS-5B, Buckinghamshire¹, England). The apparatus was set to excite the Rhodamine WT at 560 nm and to read the emission at 577 nm.

2.3. Statistical analysis

Each treatment was replicated three times using a complete randomized block design. All statistical analyses were made using SAS/STAT software package release 6.12 for Windows '95. The BTCs were statistically compared using different techniques. One of the statistical comparisons consisted of comparing the relative concentration at different PVs. Another statistical comparison was made on the parameters of the non-linear regressions used to fit the BTCs (all treatments and replicates). The regression parameters were then statistically compared. Mean separations were made using the LSD tests.

3. Results and discussion

3.1. Water movement

For the treatment where the macropore was open at both ends (O–O), water reached the lower end of the soil column about 100 times faster (0.01 PV). Therefore, the breakthrough time was shorter for O–O than that for other continuity (O–C, C–O, C–C, Control) treatments. For these continuity treatments, there was no significant difference in breakthrough time ($PV \sim 1.0$, $P = 0.30$).

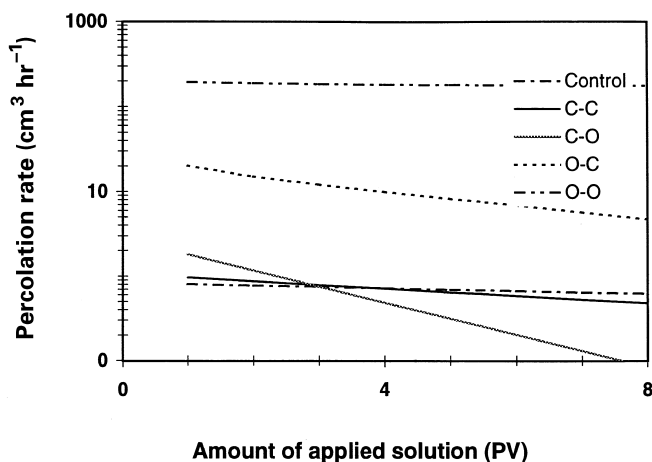


Fig. 4. Average water percolation rates as a function of the amount of applied solution (pore volume) for various macropore continuity treatments.

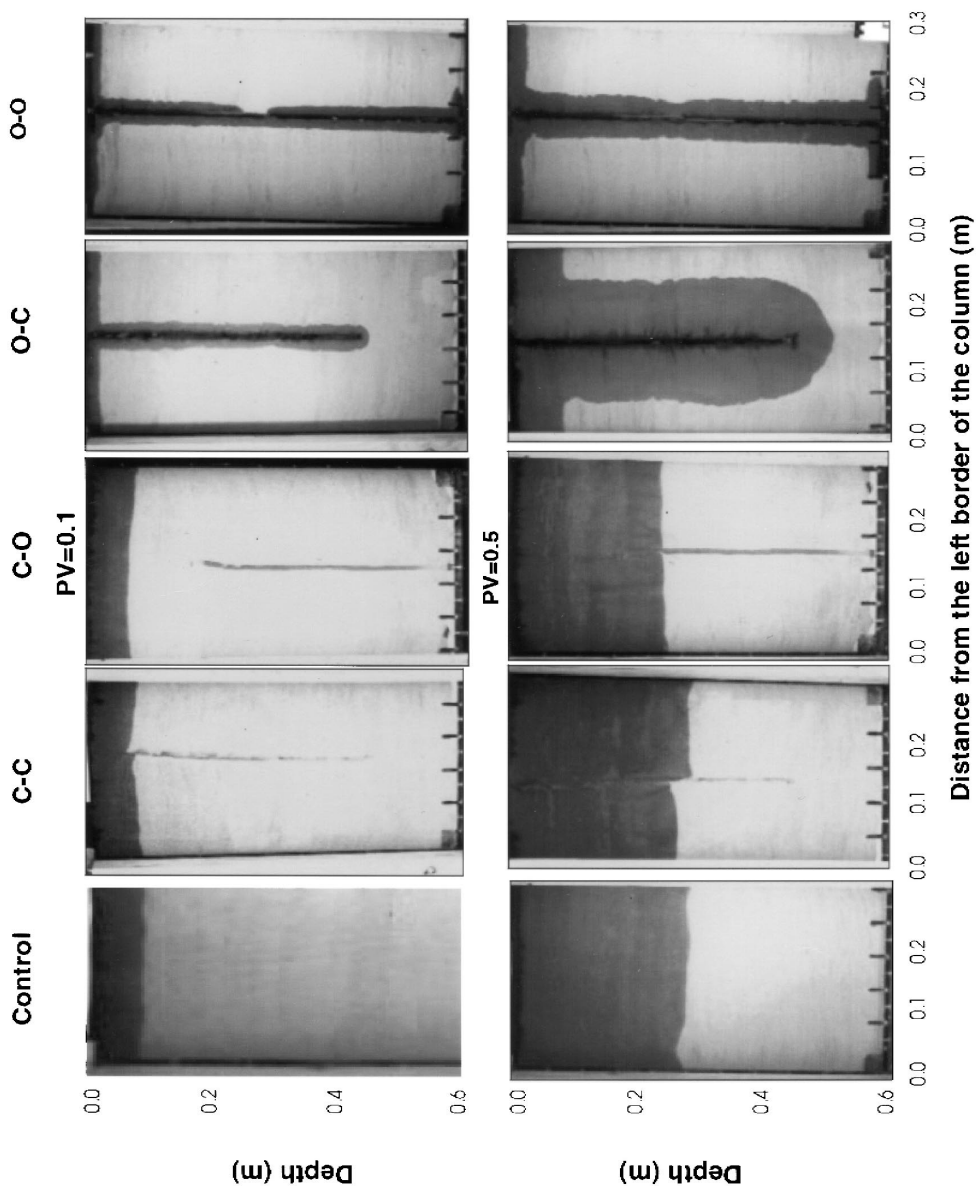
Water percolation rate with O–O macropore was two orders of magnitude higher than that of the Control treatment (Fig. 4). The percolation rate for all other continuity treatments decreased over time (Fig. 4), suggesting that even after an application of 6 PV of solution (about 15–30 days), the steady state flow condition had not been reached. This is probably due to settling of soil particles and to high clay content (25%) of the Forman loam soil that may have caused some swelling of the soil.

Water percolation rate for the O–C type of macropore was also significantly ($P = 0.001$) higher (about one order of magnitude) than that of the other continuity treatments (Fig. 4). However, no significant differences were observed in water percolation rate between the Control, C–C, and C–O types of continuity. This was expected because the macropores in the C–C and C–O treatments remained empty during the entire breakthrough run, leading to a behavior similar to that of a homogeneous soil.

Some photographs of water infiltrating into the dry soil for all continuity treatments (Fig. 5) show that the wetting front movement was similar for the Control, C–C, and C–O treatments. In these treatments, the anisotropy in water distribution was mostly in the vertical direction. These results indicate that during modeling of water percolation in macroporous soils, it may be reasonable to ignore single macropores that are closed at the soil surface.

For treatments that contained a macropore open at the soil surface (O–O, and O–C), water reached the bottom of the macropore about 100 times faster (0.01 PV) and thus bypassed a majority of the soil matrix. In these treatments, the anisotropy in water distribution at early times was mostly in the horizontal direction (Fig. 5). There was very little absorption of water away from the walls of the macropore until the macropore

Fig. 5. Water distribution patterns in soil columns of different macropore continuity types after 0.1 and 0.5 PV of solution has infiltrated into the soil (light color, dry soil; dark color, wet soil).



filled up. These observations suggest that the assumption often used in modeling — that water instantaneously reaches the lower end of the surface open macropores under ponding conditions — is reasonable.

3.2. Tracer movement

3.2.1. BTCs

The BTCs presented in Fig. 6 are made of only one replicate. The two other replicates are not presented for clarity since they gave the same results and led to the same conclusions. Each point used in the BTCs consists of a weighted average of five outlets. The weight was the volume of outflow solution. Also, for some of the samples during early times, the relative concentration of bromide was higher than 1.0, leading to a mass recovery of roughly 110%. We attribute the $C/C_0 > 1.0$ to some anion exclusion and to some interference of electrolytes from the soil solution during bromide measurements. Some evaporation of the input solution in the column chamber and some in the collecting tubes may also have occurred even though the chambers were covered with a plastic sheet and the collecting tubes had a narrow opening.

At first hand, one may expect the bromide BTC to follow the convection–dispersion types of curve. However, the dispersion occurs when a solute displaces another one and the speed of displacement changes between different pores. However, in this experiment, there was no solute to displace at the water front since the soil was dry. This resulted in a bromide concentration that remained the same as it moved. Therefore, bromide moved more like a piston flow, i.e., the relative bromide concentration was nearly 1.0 when the solute first leached out of the column in all continuity treatments.

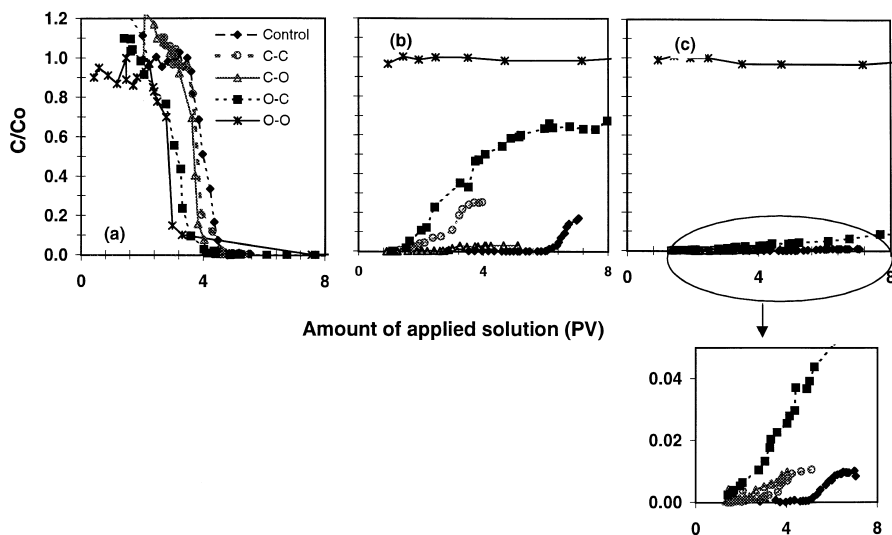


Fig. 6. Average (five outlets) BTCs of (a) Br^- , (b) Rhodamine WT, and (c) FD&C Blue #1 as influenced by macropore continuity type.

At early relative times (< 3.5 PV), bromide in O–O treatment was flushed out faster ($P = 0.001$) than in any other treatments (Fig. 6a) since the macropore was directly connected to the bottom outlet. However, the displacement was much slower in the surrounding matrix since most of the solutions were carried through the macropore, thus bypassing the soil matrix. For example, only a small fraction of the matrix was wet by the time the new input solution was introduced. In addition, the bromide BTC of the O–O treatment also showed some tailing due to a slow displacement of bromide through the matrix (Fig. 6a). The other macropore continuity treatments did not show a significant difference in the effluent bromide concentration ($P = 0.40$). There was no significant difference in the leachate concentration at later times ($P = 0.25$).

During the breakthrough experiment, the relative bromide concentration of the effluent was expected to decrease significantly faster from the O–C treatment than the Control treatment. In actual time, this decrease was an order of magnitude faster. Although there was a trend for the O–C and C–O treatments to flow faster than the Control (Fig. 6a), it was not significant in relative time ($P = 0.42$). We attributed this unexpected result to variation between replicates. Also, about 50% of the effluent solution was flowing from the outlet directly underneath the O–C macropore. In other words, the flow processes occurring in the macropore influenced more the BTC than the processes occurring in the upper soil matrix. The displacement of the old solution (high KBr concentration) with the new solution (zero KBr concentration) resulted in diffusion and mixing in the O–C macropore. The mixing alone in the macropore would lead to an asymptotic (less than proportional) decrease in solute concentration in the macropore. Additionally, there was dispersion in the matrix below the macropore (from 0.45 to 0.60 m deep) as the rest of the soil matrix and the outlets away from the macropore had a high bromide concentration. These processes together would lead to bromide movement slower than is often expected. We believe that these processes were minimal in the O–O macropore because there was no time for solute mixing and the flow was so fast that when the applied solution was changed, the O–O macropore had time to empty and the outlets away from the macropore did not flow.

In the Fig. 6a, the O–C treatment approached a zero relative concentration about 1 PV earlier than in the Control treatment. This difference was not significant as this effect was observed in only two replicates, whereas the third replicate was slightly slower than the Control.

Nearly similar BTCs of bromide for the C–O, C–C and the Control treatments (Fig. 6) with a homogeneous distribution of solute outflow between all outlets (data not shown) suggest that solute movement through the soil matrix was more important than through the macropores for these continuity types. All three replicates were consistent.

Sigmoidal shape of BTC is the result of random solute dispersion. Gerritse (1996) suggested that a deviation from sigmoidal shape could be due to the presence of heterogeneous adsorption sites in the soil. Bosma and Van der Zee (1993) indicated that another reason for non-sigmoidal shape BTC could be the non-equilibrium adsorption of tracers during leaching. The BTCs of Rhodamine WT were not sigmoidal (Fig. 6b). Except for O–O treatment, the shape of the Rhodamine WT BTCs appears to be more like a negative exponential function similar to the one observed by Gerritse (1996) and Bosma and Van der Zee (1993) for heterogeneous sites or for non-equilibrium condition.

In our experiment, heterogeneous adsorption sites could have occurred because of a possible sorting of soil particles along the macropore walls compared to the rest of the profile. It is also likely that non-equilibrium adsorption occurred in our experiment. The flow in the macropore was fast and thus, the tracers probably did not have enough time to fully equilibrate with the soil along the macropores. Additionally, Allaire-Leung et al. (1999) showed that the adsorption of Rhodamine WT decreases with a decrease in the concentration of potassium bromide. Since the bromide concentration in this experiment continually changed during the breakthrough experiment (Fig. 6a), it is likely that the adsorption of Rhodamine WT continuously changed and was never at equilibrium in our soil columns. The above analysis suggests that deviation in the shape of the Rhodamine WT BTCs from sigmoidal was probably due to both non-equilibrium adsorption condition and heterogeneous adsorption sites. Concentrations of the FD&C Blue #1 in the leachate were not high enough to obtain complete BTCs. It is thus unknown how the BTCs of FD&C Blue #1 deviated from the expected sigmoidal shape.

The Rhodamine WT (Fig. 6b) and FD&C Blue #1 (Fig. 6c) moved fastest through the O–O treatment, followed by O–C, C–C, C–O, and the Control treatment. The breakthrough time of both dyes (0.01 PV) in the O–O types of continuity was two orders of magnitude smaller than that of the Control (4.4 PV) treatment (Fig. 6b,c). This is similar to the observation of Shipitalo et al. (1994), who observed that closed macropores at the surface were least whereas open macropores at the surface were most efficient in transport of solute through soils.

The relative concentration of Rhodamine WT in the effluent at 1.0 PV was one order of magnitude higher ($P = 0.0001$) for the O–C (0.02 C/Co) than for the C–O, C–C, and the Control treatment (0.002 C/Co). Similarly, the concentration of FD&C Blue #1 at 1 PV (0.02 C/Co) for the O–C type of macropore was more than two orders of magnitude higher ($P = 0.0001$) than that in the Control treatment (< 0.001 C/Co). At any PV, the relative concentration of Rhodamine WT and FD&C Blue #1 in the C–O treatments was not significantly different from that of the Control treatment (Fig. 6). These results indicate that macropore continuity influence was greater on FD&C Blue #1 than on Rhodamine WT movement.

3.2.2. Apparent retardation factor

The apparent retardation factor of both dyes was most affected by the O–O type macropores when compared to the Control treatment (Table 1). Both dyes moved as fast as the water in the O–O treatment, thus giving an apparent retardation value of 1.0. This is because the applied solution directly entered the macropore that carried it to the lower end of the column without any significant tracer adsorption.

The O–C and C–C type of macropores also showed a significant decrease in the apparent retardation values of Rhodamine WT as compared to the Control treatment (Table 1). The apparent retardation of FD&C Blue #1 in O–C treatment was six times smaller than that of the Control treatment. Comparatively, the apparent retardation factor of Rhodamine WT for the same treatment was five times smaller than that of the Control treatment (Table 1). The reasons for O–C type of continuity to have a low R' are similar to that of the O–O treatment. For the C–O and the C–C treatments, we believe that this is due to a small bypassing of the soil matrix by the solution along the inside wall of the

Table 1

Effect of macropore continuity on apparent retardation factor (R') and depth to the center of mass of Rhodamine WT (RWT) and FD&C Blue #1 (Blue) after 8 PV has passed through the soil

LSD = Least significant difference at confidence level $\alpha = 0.05$.

Continuity treatments	R'		Depth to the center of mass (m)	
	RWT	Blue	RWT	Blue
Control	5.52	13.0	0.21	0.06
C–C	2.31	9.05	0.20	0.09
C–O	4.66	10.3	0.13	0.07
O–C	1.07	1.97	0.29	0.28
O–O	1.00	1.00	0.33	0.32
LSD	2.30	3.84	0.09	0.13

macropore. A very thin flow along the macropore wall was observed during the breakthrough experiment. In the case of C–O macropore, the same process occurred but some solution slowly dropped from the outlet directly connected to the macropores so that a small, but not significant, bypass occurred and the macropore remained empty.

3.2.3. Concentration distribution

The center of mass for both Rhodamine WT and FD&C Blue #1 was significantly deeper in the soil profile for the O–O and the O–C type macropores compared to the other treatments (Table 1). This suggests that under transient ponded conditions, macropores that are open at the soil surface are important pathways for chemical movement to deeper depths. These findings are similar to the conclusion of Trojan and Linden (1994), who showed that earthworm macropores were the primary pathways for carrying Rhodamine WT below 0.2 m depth in the field.

In the Control treatment, the depth to the center of mass of FD&C Blue #1 was significantly ($P = 0.01$) closer to the surface (0.06 m) than that of the Rhodamine WT (0.2 m). However, for the O–C and O–O treatments, the depths to the center of mass for both dyes were about the same (≈ 0.3 m). These results suggest that macropore continuity was more important in carrying FD&C Blue #1 than the Rhodamine WT. Thus, the importance of macropore continuity increases with an increase in the adsorption coefficient of the tracer.

Concentration profiles of FD&C Blue #1 in the Control, C–C, C–O, and O–C treatments show that most of the dyes were in the first few centimeters of the column (Fig. 7). There were a few replicates where some penetration of the dyes occurred to a depth of 0.2 m. Although not obvious in Fig. 7, the bulk mass in O–C treatment was in the top few centimeters. This is similar to the findings of Flury et al. (1995), who observed that the bulk of herbicides was in the top soil even though some chemicals had bypassed the soil matrix. The exception to the above observation was the O–O treatment, where the bulk of the tracers was at deeper depth and alongside the macropore (Fig. 7). The Rhodamine WT had distribution patterns similar to that of the FD&C Blue #1 except that the Rhodamine WT penetrated to deeper depth (data not shown).

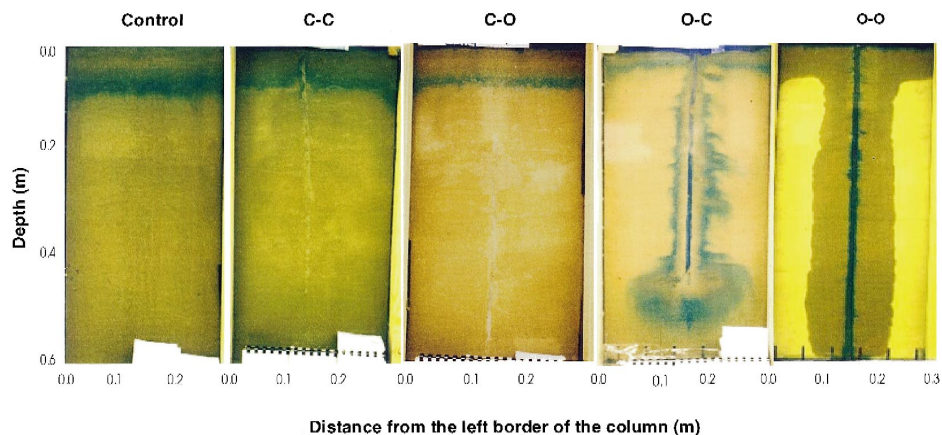


Fig. 7. Stained pathways showing the influence of macropore continuity on movement of FD&C Blue #1 after 4 PV of solution has infiltrated into the soil columns.

For O–O and O–C treatments, there was less dye near the upper end of the macropores than at the lower end. This suggests that the dye moved laterally into the soil mostly from the lower end of the surface open macropores. Since the macropores in these treatments were vertically positioned, there was a large dye concentration gradient in the horizontal direction. This suggests that under transient flooded conditions, solute movement in a soil containing macropores that are open at the soil surface could be modeled such that (1) the applied solution reaches the lower end of the macropore within a short time, and (2) then, the solute penetrates deeper and laterally into the soil matrix from the macropore.

3.3. Influence of neighboring macropores

In Section 2, the impact of macropore continuity was studied using a single macropore per column except for the Control treatment that did not contain macropore. Usually, a single macropore does not occur by itself in nature. There are other macropores in its vicinity and they may interact with each other. This experiment was designed to assess the impact of macropore continuity in the presence of a neighboring macropore.

Bromide BTC was only slightly affected by the type of macropore population, spacing, and orientation in comparison to the Control treatment (Fig. 8a). There was a slight delay in the breakthrough of Rhodamine WT and FD&C Blue #1 in the Mixed population treatment as compared to the Control treatment. This delay was mostly due to two macropores in the Mixed population treatment that were inclined and thus, their lower end was not as deep as the lower end of the vertical macropores of the Control treatment (Fig. 3).

The BTC results, as such, do not allow definitive conclusion on the impact of neighboring macropores on the importance of macropore continuity. However, one could deduce such importance by studying the distribution of tracer concentration between different outlets (Fig. 9) and by studying the dye distribution profile (Fig. 10).

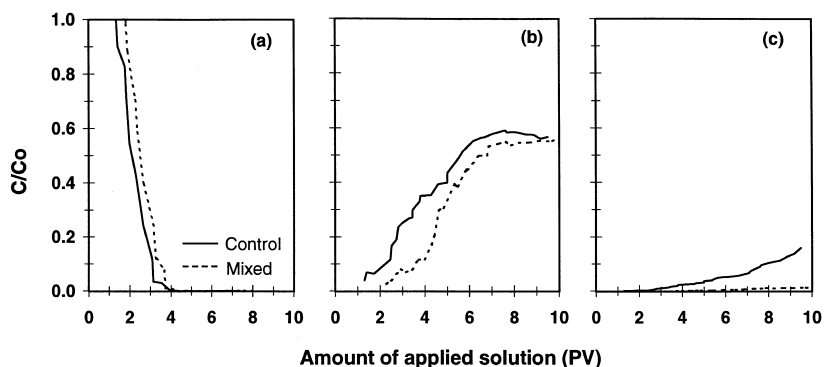


Fig. 8. Average (three replications and 15 outlets) BTCs of (a) Br^- , (b) Rhodamine WT, and (c) FD&C Blue #1 as influenced by macropore population.

The distribution of concentration along the lower border of the column for all tracers clearly indicate the position of the macropores as the concentration increased right below the macropores. For the mixed treatment, the pattern was somewhat more complex, but the position of the macropores could also be deduced. For example, the Rhodamine WT at 3.5 PV shows a double peak between 0.3 and 0.5 m for the left

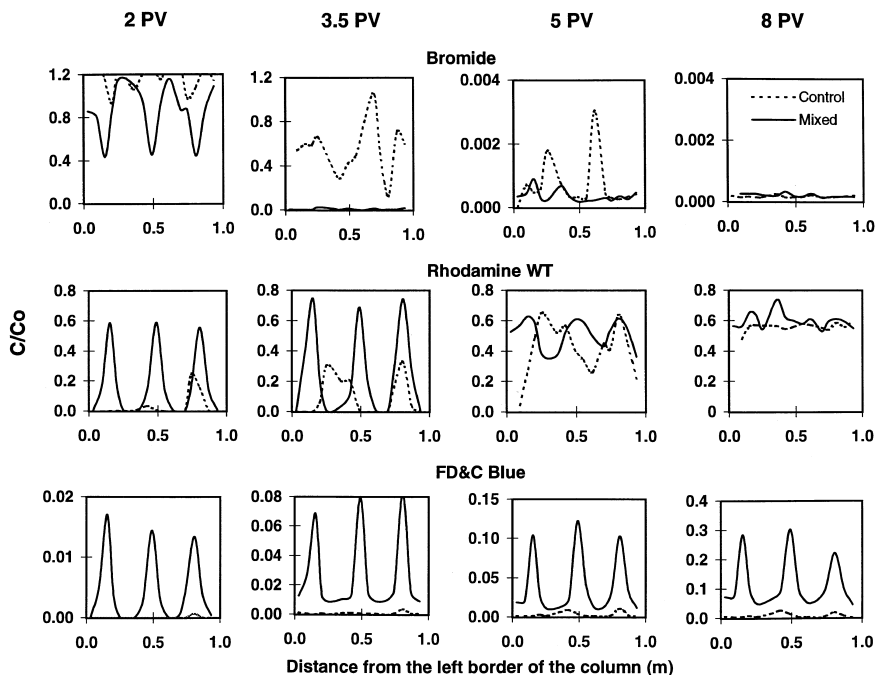


Fig. 9. Distribution of (a) bromide, (b) Rhodamine WT, and (c) FD&C Blue #1 along the lower boundary of the column (15 outlets) at different relative times and for two macropore populations.

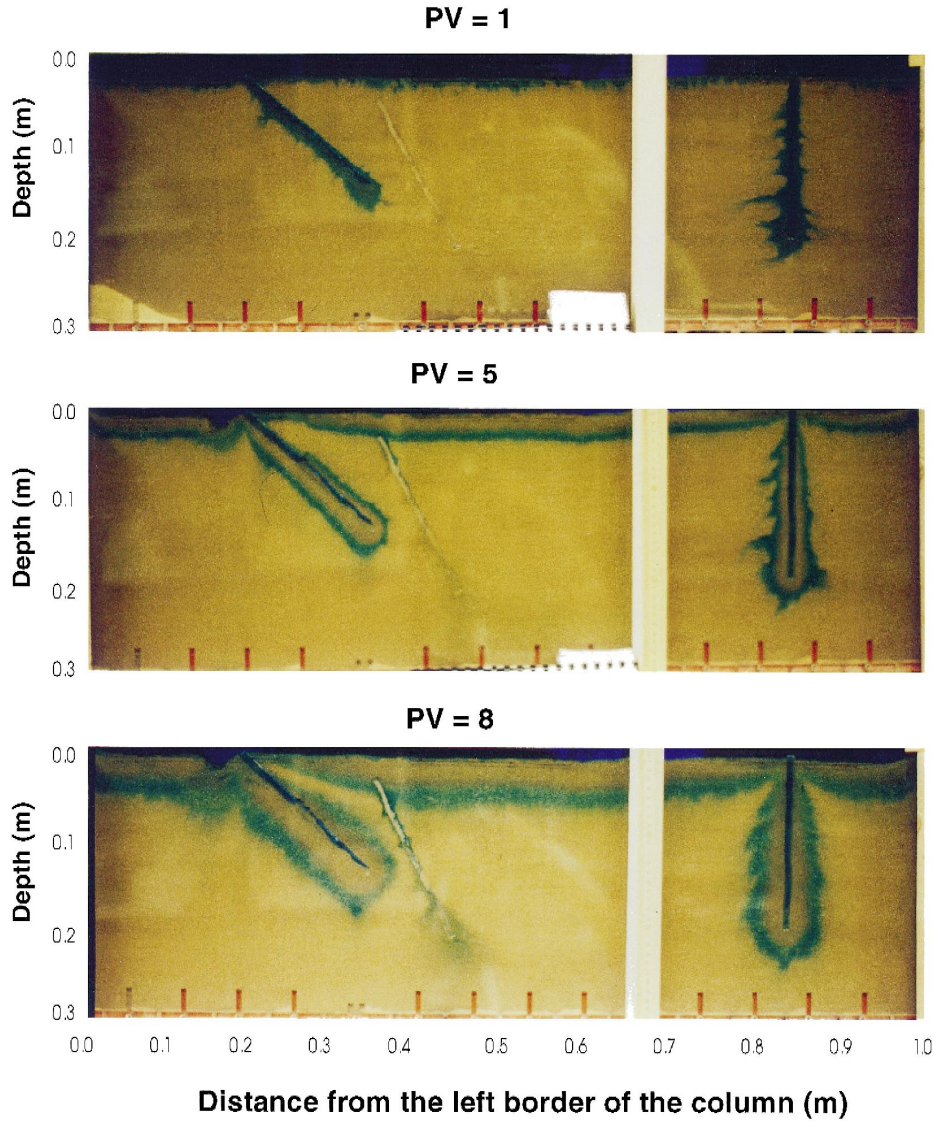


Fig. 10. Stained pathways showing the influence of a mixed macropore populations on the movement of FD&C Blue #1.

border of the column (Fig. 9b). If we did not know the distribution of macropores, we could have interpreted the double peak as the result of interacting macropores or a macropore with a complex shape. Therefore, the effect of the macropore population on the solute movement is more obvious on this figure than from the BTCs. This figure also shows that the sampling position has to be considered when running BTCs with undisturbed or repacked soil columns in the laboratory. If a single outlet is used to

sample the leachate, then significant information is lost on preferential flow and on heterogeneity.

Based on the previous experiment, the C–C macropore was not expected to carry much chemical down into the profile. However, Fig. 10 shows that the C–C macropore favored preferential flow of dyes to deeper depth. These results suggest that contrary to the general belief, all types of macropore continuity, even C–C, can be important to consider when studying solute transport in macroporous soils.

The mechanism by which the C–C macropore favored preferential movement of solute in the Mixed population treatment could be described as a three-step process. (1) The O–C inclined macropore directed the solute to flow toward the C–C type macropore, i.e., it altered the flow path of water (Fig. 10; PV = 1). (2) Then, a film of solution flowed along an outside wall of the inclined C–C type macropore. This process was visually apparent during the experiment (Fig. 10; PV = 5). (3) Finally, the C–C macropore favored the movement of dyes similar to the process of funnel flow (Fig. 10; PV = 8). Kung (1993) has shown that funnel flow in soil occurs if the solution meets a layer of a coarser soil, if the boundary where a fine layer meets the coarse layer is inclined, and if the unsaturated hydraulic conductivity of the coarse layer is much higher than the hydraulic conductivity of the overlain finer soil. In our set-up, the C–C macropore acted like a coarser layer whereas the soil matrix was the fine layer. In other words, there was a boundary of a fine layer over a coarse layer at the soil matrix–macropore interface. Since the C–C macropore was slightly inclined (12%), the combination of the above conditions forced the start of a funnel flow. Like in funnel flow, we also observed solution flowing along the upper wall of the macropore (Fig. 10; PV = 8).

4. Conclusions

The conditions used in this study were extreme in comparison to the real world. Flooded irrigation over an initially dry field, sudden rainfalls over a dry field such as in southern California, sudden flood in dry land from an overflowing river, and water infiltration from snow melt when the soil was dry in the fall prior the snowfall may be some examples of conditions similar to this experiment. The conditions were chosen so that if a certain type of macropore did not influence much the solute movement, then we believe that this type of macropore will not be important under any conditions (wetter soil, small rainfall) when the solute is applied at the soil surface. The results of this experiments suggest the following conclusions and practical implications.

(1) Depending on the continuity to the soil surface and to the lower end of the column, macropores do not always favor faster movement of solute through soil.

(2) Macropore continuity is an important variable that should be included in modeling chemical transport for macroporous soils. If simplifications have to be made, then C–C and C–O macropores could be neglected unless there are other macropores in their vicinity. Macropores that are open at the surface (O–O and O–C) cannot be neglected while modeling solute transport in soils under saturated flow condition.

(3) The importance of macropore continuity seems to increase with an increase in the adsorption characteristics of the tracer. A tracer should be chosen with adsorption

characteristics similar to that of the contaminant under study. For a conservative tracer, the continuity effects of C–C, C–O, and O–C type macropores can be neglected.

(4) The presence of another macropore in the neighborhood can lead to interactions between macropores and in turn enhance the importance of macropores. Under these conditions, even the C–C type of macropores may become an important flow path for transport of chemicals to deeper depths.

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