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# FLOW SEPARATION IN UNDISTURBED SOIL USING MULTIPLE ANIONIC TRACERS. PART 2. STEADY-STATE CORE-SCALE RAINFALL AND RETURN FLOWS AND DETERMINATION OF DISPERSION PARAMETERS

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## ABSTRACT

A series of experiments designed to study the separation of flow components from two large undisturbed cores under steady-state rainfall (downward) and return (upward) flows under near-saturated conditions is summarized. The experiments were conducted on soil columns collected from Lancaster University and the Slapton Wood catchment, Devon. The use of the relatively conservative tracers, potassium bromide, *o*-(trifluoromethyl)benzoic acid and 2,6-difluorobenzoic acid and a combination of application rates made it possible to quantify the different sources of water contributing to the discharge hydrographs. There is significant retention of tracer within the cores, despite the application of several pore volumes of water.

The use of steady flow conditions allowed the determination of dispersion coefficients, dispersivity and proportion of 'mobile' water content parameters of the advection–dispersion equation. It was found that there were significant differences between the dispersivities at different flow-rates under upward and downward flux conditions and that in the undisturbed cores studied here the apparent proportions of mobile pore water ranged between 0·33 and 1·0, with an apparently complex relationship to flux rate. Prediction of transport in undisturbed soil remains problematic and tracer experiments will continue to be needed to provide a fundamental understanding of the complex flow processes involved.

KEY WORDS anionic tracers; soil water; solute transport; multicomponent mixing; breakthrough curves; undisturbed soil columns

## INTRODUCTION

Part 1 of this series (Reeves *et al.*, this issue) has outlined the use of multiple fluorobenzoate and bromide tracers in the study of soil water movement, as pioneered by Bowman (1984), describing both the high performance liquid chromatography (HPLC) analysis techniques and the multiple flow component separation that is made possible by the use of multiple tracers. By using chemical tracers to label separate flow sources it is possible to quantify the relative importance of each source to the discharge hydrograph. This enables the assessment of the nature of flow pathways and the degree of mixing occurring between the different flow sources. In this paper these techniques are applied to the study of steady-state flows through three undisturbed soil columns.

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In the experiments outlined, flow occurs within a finite soil column. Two types of steady inputs are used: 'return flow' into the column base and simulated rainfall onto the soil surface. The use of chemical tracers allows the input water to be distinguished from water stored in the column before an application ('old' water) in the discharge at different times during any one event. From this information it is possible to conceptualise the flow processes in operation and how these respond to changes in the driving forces and the boundary conditions. Reeves *et al.* (this issue) showed how contributions to the column outflow from different sources could be distinguished, but it is also possible to discriminate between two flows from the same source, which are applied at different times labelled with different tracers, and therefore quantify the effects of two events in series.

A fundamental assumption made about the system is that the initial concentration of a tracer being used to identify the flow from any given source is zero within the soil column before the input of the tracer. Given the way that tracers are repeatedly used in these experiments, this condition is not strictly achieved. However, this problem is normally minimized by the use of different tracers in successive experiments and the application of at least one pore volume (core volume * estimated porosity) of tracer-free water as return flow immediately following the applied pore volume of tracer solution. The resulting background concentration of tracer in the effluent is then always low ($< 1{\cdot}0\,\mathrm{mg\,l^{-1}}$). However, as shown in Part 1, the retention of labelled water within the column at the end of an experiment can be significant. This then allows the opportunity to follow the output of that tracer during later discharges, remaining aware, of course, that the longer the tracer is retained in the column, the greater is the possibility of tracer concentrations being affected by diffusive exchange with unlabelled water stored in the column and/or degradation and time dependent sorption. All of these processes will tend to reduce the effective concentration of the labelled water and lead to a reduction in the estimation of the outflow contribution of that labelled component.

The mixing equations for multiple components have been discussed by Reeves *et al.* (this issue). Where it can be assumed that background concentrations of the tracers will be negligible the proportion of the old water component in the discharge at any time can be calculated as

$$Q_0 = Q\,(1 - \Sigma\, C_i/C_i^o)$$

where $C_i$ is the concentration of that tracer at the given time and $C_i^o$ is the concentration of tracer in the applied water. Reeves *et al.* (this issue) point out that the accuracy of these calculations depends only on the precision with which the ratios $C_i/C_i^o$ represent the discharge components. Sorption and diffusion, if they occur, will tend to reduce the measured concentration for each component and lead to an overestimate of the proportion of old water in the total discharge. Processes such as the co-elution of soil-derived substances with the tracer in the HPLC column will have the opposite effect, leading to an underestimate of the proportion of old water. Later desorption of sorbed tracer could lead to an overestimate of the proportion associated with a particular tracer at longer times.

## EXPERIMENTAL METHODOLOGY

Large, undisturbed soil cores were extracted as described in Part 1 of this series from sites on the Lancaster University campus (core LUW2) and from grassland and woodland sites in the Slapton Wood catchment (cores SLG and SLW, respectively). The dimensions of the cores are given in table IV of Part 1. The cores were sealed using fibreglass and resin and mounted on aluminium supports above a high permeability Vyon porous plate. Water could be supplied to both the bottom and top of the cores as return flow and rainfalls at steady rates controlled by peristaltic pumps. As before, an even coverage of surface-applied tracer was ensured by using a moveable sprinkler with hypodermic needle drop-formers. Outflow discharges were collected from either the bottom or the top of cores using a computer-controlled Rock and Taylor interval water sampler. A full summary of the experiments reported here is given in Table I.

### *Steady-state return flow experiment: Lancaster core LUW2*

The purpose of this experiment was to explore the nature of steady upward return flow in an undisturbed soil core, with cracks and root channels, using three applications of potassium bromide at different

Table I. Details of steady-state rainfall and return flow experiments

| Experiment | Tracers | Concentration ($mg\,l^{-1}$) | Application rate ($ml\,h^{-1}$) | Duration (h) | Darcian flux ($cm\,h^{-1}$) | Estimated pore water velocity ($cm\,h^{-1}$) |
|---|---|---|---|---|---|---|
| Return Flow | | | | | | |
| LUW2 A | KBr | 100 | 1060 | 11 | 1·45 | 3·22 |
| | *o*-TFMBA | 20 | | | | |
| | 2,6-DFBA | 30 | | | | |
| LUW2 B | KBr | 100 | 534 | 22 | 0·731 | 1·62 |
| LUW2 C | KBr | 100 | 252 | 44 | 0·345 | 0·77 |
| SLG A | KBr | 100 | 1000 | 18 | 1·37 | 3·04 |
| SLG B | *o*-TFMBA | 28·9 | 500 | 36 | 0·68 | 1·52 |
| SLG C | *o*-TFMBA | 19·5 | 250 | 72 | 0·34 | 0·76 |
| SLW A | KBr | 70.0 | 1000 | 18 | 1·37 | 3·04 |
| SLW B | KBr | 105.0 | 500 | 36 | 0·68 | 1·52 |
| SLW C | KBr | 105·52 | 250 | 76 | 0·34 | 0·76 |
| Rainfall | | | | | | |
| SLG D | KBr | 100 | 256 | 67 | 0·35 | 0·78 |
| SLG E | 2,6-DFBA | 28·9 | 136 | 135 | 0·19 | 0·41 |
| SLW D | KBr | 97·98 | 1000 | 18 | 1·37 | 3·04 |
| SLW E | KBr | 100·48 | 500 | 36 | 0·68 | 1·52 |
| SLW F | KBr | 96·85 | 250 | 77 | 0·34 | 0·76 |

flow-rates. During the first application 2,6-DFBA and *o*-TFMBA were also added to determine comparative breakthrough curves (see Table I). The results are shown in figure 6 of Reeves *et al.* (this issue).

Water was supplied into the base of the core using a peristaltic pump to achieve flow-rates of approximately 1 000, 500 and 250 $ml h^{-1}$. For each flow-rate, steady state was established by pumping deionized water through the system before the introduction of a tracer pulse. Tracer flow was introduced for a period necessary to displace one pore volume of fluid. Following the input of the tracer the flow was switched back to deionized water for another pore volume of water to 'flush out' the soil. This technique facilitates an examination of the processes of water movement within the core during steady flow and especially the relative importance of mechanisms such as convection, dispersion, diffusion and by-passing by macropore flow at different flow velocities. Table I gives details of each section of the experiment.

The discharge overflowing from the column surface was collected in the interval water sampler. Collection intervals between samples were constant for each section, 30 minutes for the first two sections and 60 minutes for section C. A subsample of effluent (10 ml) was taken from each water bottle and was analysed for the input tracers using HPLC techniques detailed in Part 1.

### *Steady-state return flow experiment: Slapton grassland core SLG*

The experiment consisted of three sections each with a distinctive flow-rate. For each section there was an equilibration period, where the flow within the core was allowed to steady to a constant rate. At this stage, a pore volume of water containing a known concentration of tracer was pumped up through the column at a steady rate controlled by a peristaltic pump. The flow-rates were sufficient to keep the soil column at or close to saturated conditions. The flow was switched back to water after the tracer solution had been added. This marked the end of one section of the experiment and was followed by a reduction in flow-rate, gradually taking the flow in the column to a new steady state. In this case the use of the same tracer in sections B and C of the experiment precludes an accurate separation of the discharge into components associated with each tracer addition.

### *Steady-state rainfall experiment: Slapton grassland core SLG*

Initially, the soil core was saturated and then allowed to drain for 48 h. Water was then added from the rainfall sprinkler until a steady flow was achieved. Approximately one pore volume of tracer was added, followed by a further pore volume of unlabelled water. During this application the rainfall rate was changed to a lower value and the flow allowed to stabilize before the addition of a pore volume of the second tracer. This was then followed by a further pore volume of unlabelled water at the lower application rate. Table I shows the details of each section of the experiment. It was found that 250 $\mathrm{ml h^{-1}}$ was close to the highest application rates that could be used without the development of water ponding on the surface. Discharge was collected from the base of the column.

### *Steady-state return flow experiment: Slapton woodland core SLW*

Batch absorption tests suggested that for this core the fluorobenzoate tracers could not be considered to be conservative tracers, presumably due to complexation with organic matter in the soil. In this case therefore only bromide could be used as a tracer, restricting the accuracy of any hydrograph separations. The experiments were carried out in a similar manner to the Slapton Grassland core with three contiguous sections of progressively lower application rates and discharge being collected as overflow from the soil surface.

### *Steady-state rainfall experiment: Slapton woodland core SLW*

It was found that the Slapton woodland core could support much higher rainfall application rates without the build-up of ponding at the surface. The same three application rates were used as for the return flow experiments. Discharges were collected from the base of the sample.

## RESULTS AND DISCUSSION

### *Steady-state return flow experiment: Lancaster core LUW2*

A composite diagram of the tracer output from all three sections of the experiment is shown in Figure 1. The cumulative breakthrough curves for the three tracers used in section A of the experiment may be seen in more detail in Figure 6 of Part 1. The use of bromide tracer in each of the three sections of the experiment precludes the separation of discharge into components associated with each of the inputs. Figure 1 suggests that there may be some carry-over of bromide tracer between the inputs, despite the addition of one pore volume of unlabelled water between each input. This is confirmed to some extent

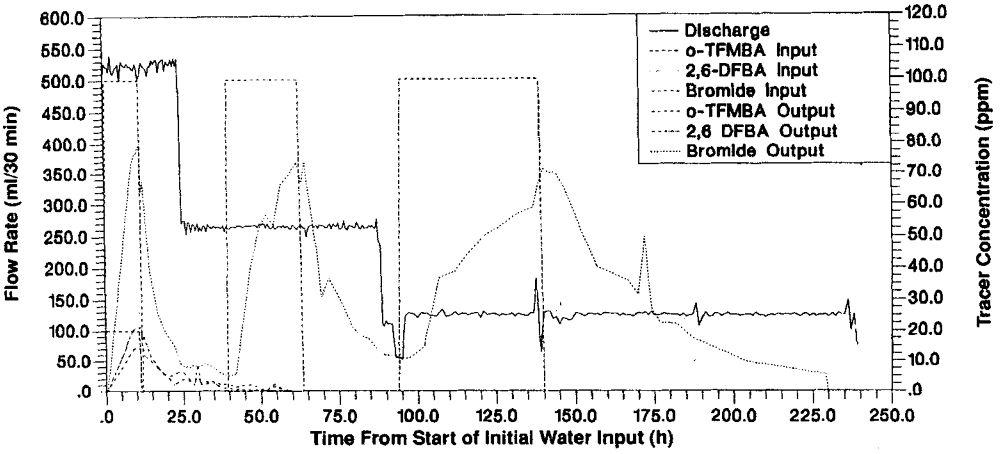

Figure 1. Discharge and tracer input and output concentrations during the steady-state return flow experiment on the Lancaster soil core (LU1)

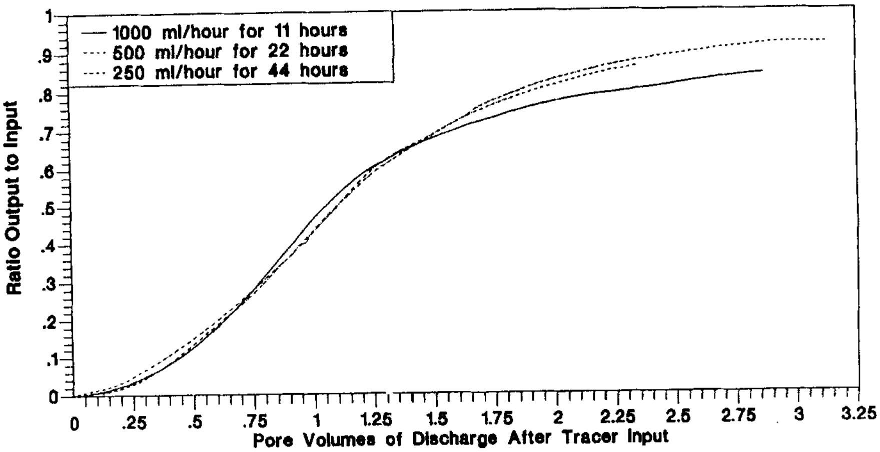

Figure 2. Breakthrough curves for each bromide input during the steady-state return flow experiment on the Lancaster core (LU1)

by plots of the cumulative breakthrough curves for each section of the experiment plotted with a time-scale of pore volumes (Figure 2), which show that only 0·84 of the first input is seen in the discharge from the column before the next addition of bromide (after 2·85 pore volumes). Sections B and C both show similar cumulative breakthrough curves, reaching over 0·9 of the mass input. All three breakthrough curves are similar up to 1·5 pore volumes, showing a similarity is the dispersive behaviour at different flow-rates. The dispersion is high; there is a very rapid breakthrough in each case, while half the input mass is discharged by a cumulative outflow of 1·1 pore volumes.

These cumulative curves indicate that there is net retention of bromide in the column, of the order of 0·1 of the mass added. The difference between the cumulative breakthrough curves for the three sections suggests that some of this mass is held in a dynamic storage, flushed out (or perhaps desorbed) by later inputs. The remainder however is clearly held in either physical or chemical storage for considerable periods of time.

*Steady-state return flow experiment: Slapton grassland core SLG*

Figure 3 gives details of the discharge overflowing from the surface of the core and the tracer inputs and outputs over time for all three sections of the experiment. The extremely rapid initial variations in

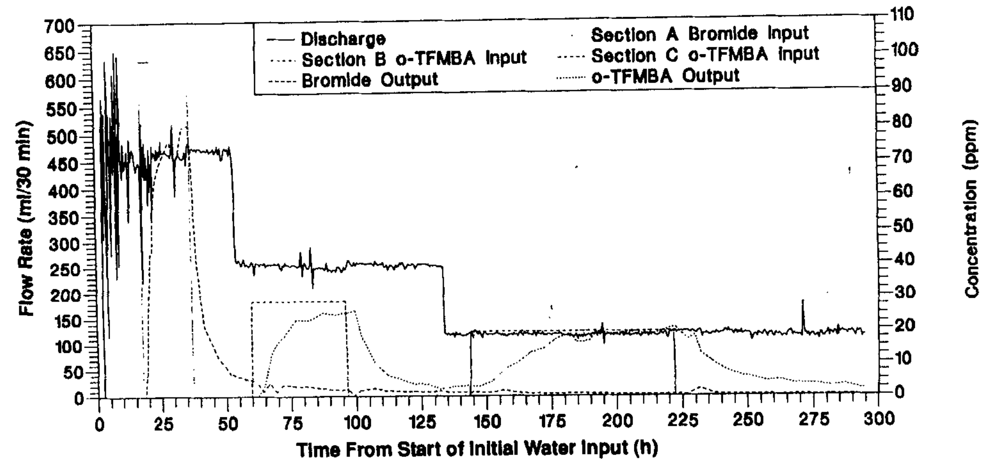

Figure 3. Discharge flow-rate and tracer input and output concentrations for the steady-state return flow experiment on the Slapton pasture core (SLG)

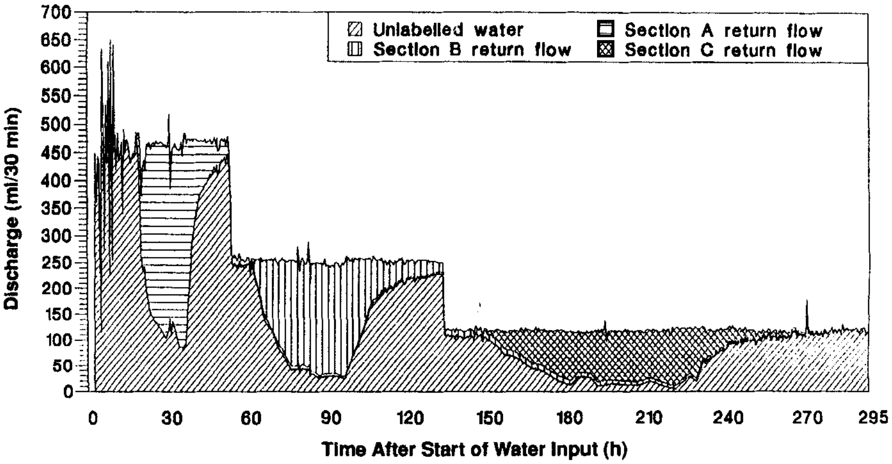

Figure 4. Separation of total discharge into unlabelled water and labelled return flow water for the steady-state return flow experiment on the Slapton pasture soil core (SLG)

discharge from the core as it wets up from a drained state has been a feature of many of our experiments with undisturbed cores. It is indicative that the flow pathways are initially significantly affected by entrapped air, leading to a pulsing of the discharge, including discharges that are significantly greater than the application rate as flow pathways are blocked, become pressurized and then open again. There is no reason to suppose that all the air is eventually removed from the column; almost certainly some residual air remains trapped in the soil matrix as the main preferential flow pathways, which may be highly localized, become established (see also the results of Levy and Germann, 1988).

Initial tracer breakthroughs are very rapid; 0·5 h for section A, 2.5 h for section B and 3.5 h for section C. These are equivalent to maximum pore water velocities through the sample of 1·1, 0·22 and 0·16 ml h$^{-1}$ respectively. The equivalent volumes of tracer labelled water before initial breakthrough are 0·03, 0·07 and 0·05 pore volumes respectively, demonstrating the preferential nature of the flow, particularly at the higher flow-rates.

Also evident from Figure 3 is the very long tail in the concentration curve for bromide, which extends throughout the full extent of the experiment. Yet calculating the cumulative output of bromide reveals that even after the application of 5·2 pore volumes of water, 15% of the added bromide remains in the column. For the *o*-TFMBA tracer only 5% is retained before the next application of this tracer in section C (suggesting less sorption of this tracer for this soil relative to the Lancaster core, but this then increases to 24% for the last section with the lower flow-rate when a sorption argument would suggest that there would be a greater output (as was the case of the bromide in the Lancaster core). Is this indicative of greater sorption at lower flow rates, or greater storage in the primary (matrix) porosity (including diffusion effects), or both? Certainly, these results indicate that the nature of solute retention and solute exchange between matrix and preferential flow pathways may be very difficult to predict in detail.

Figure 4 shows a separation of the total discharge into components associated with the different tracer inputs and unlabelled water (including 'old' water stored in the column before the experiments which cannot be distinguished from unlabelled water applied later).

Figure 5 shows the cumulative output curves for the three sections of the experiment, showing the higher retention associated with the bromide and second *o*-TFMBA applications. There is some delay in the initial part of the breakthrough curves for *o*-TFMBA relative to the bromide, again suggesting that this tracer may be slightly more susceptible to sorption within the column.

### *Steady-state rainfall experiment: Slapton grassland core SLG*

In this case only two application rates were used, each with different tracers. Figure 6 shows the discharges from the base of the column together with the input and output tracer concentrations. Note again

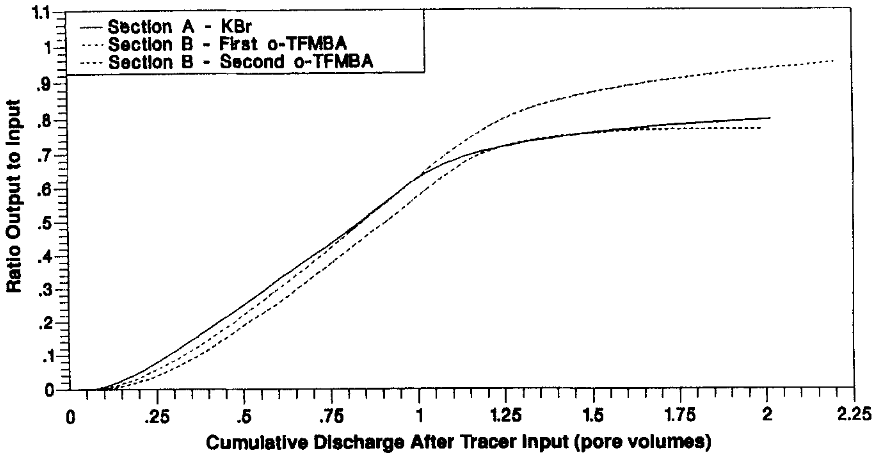

Figure 5. Breakthrough curves for the three tracer inputs of the steady-state return flow experiment on the Slapton pasture core (SLG)

the very rapid fluctuations in discharge in the initial part of the experiment. No tracer was added until these fluctuations had become less marked. Initial breakthroughs were again rapid for this vertical downward flow: 1·5 h (0·02 pore volumes) for the higher flow-rate, 10 h (0·07 pore volumes) for the lower flow-rate. The equivalent maximum pore water velocities were 0·37 and 0·06 ml $h^{-1}$ respectively. Breakthrough times were longer and maximum pore water velocities were slower for these downward flows than for return flow at similar flow-rates (sections C and D).

The cumulative mass of tracer recovered, relative to the mass input, was 1·08 in section D and 0·87 in section E. This suggests that some of the 15% of the bromide tracer retained in the return flow experiments is now appearing in section D, even after the large volume of water that has been applied since the original bromide application of *o*-TFMBA tracer is also seen in the outflow during the rainfall experiments; in fact, 93% of that calculated as remaining in the column at the end of the return flow experiments appears in these rainfall experiments, albeit at fairly low concentrations. If, for the sake of argument, it is assumed that the same proportion of the retained bromide is discharged in the rainfall experiments (although with its apparently longer retention times the proportion could be smaller), then a minimum of 90% of the bromide labelled rainfall is seen in the discharge associated with sections D and E. These results

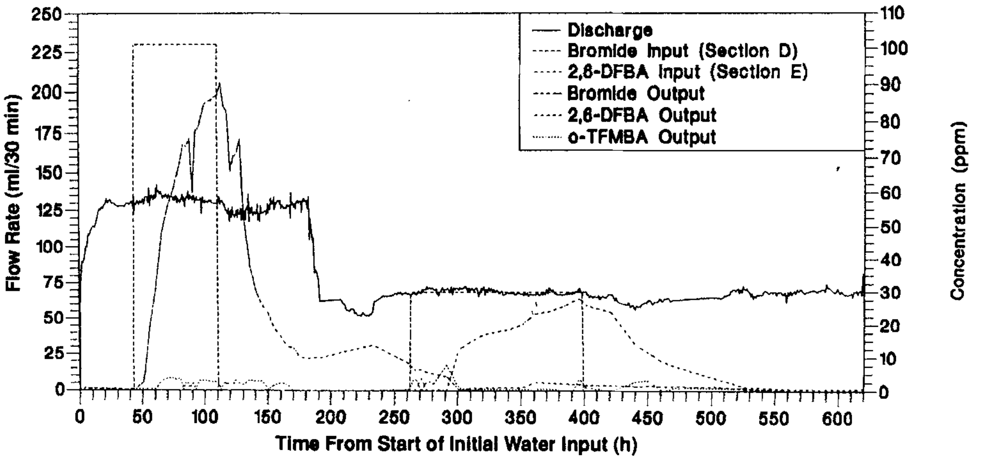

Figure 6. Discharge and tracer input and output concentrations during the steady-state rainfall experiment on the Slapton pasture core (SLG)

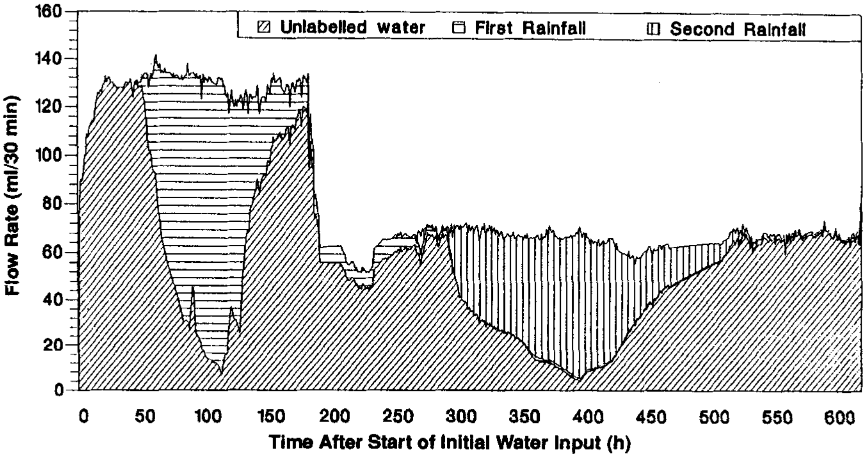

Figure 7. Separation of total discharge into unlabelled water and sections D and E rainfall for the steady-state rainfall experiment on the Slapton pasture soil core (SLG)

illustrate the very slow and persistent exchange of tracers from immobile or very slow mobile pore water (or adsorption sites?) to water in the main flow pathways.

Figure 7 shows the separated discharge hydrograph for the two sections of the experiment and Figure 8 the cumulative tracer breakthrough curves. Initially, both tracers show similar breakthrough curves, suggesting that the output of retained bromide may be delayed to the later part of the curve exchanging only with the slower flow pathways. The majority of the 'flushed out' *o*-TFMBA was seen between 0·3 and 1·8 pore volumes after the application of the bromide tracer.

*Steady-state return flow experiment: Slapton woodland core SLW*

Again, rapid fluctuations of discharge were seen in the initial stages of the experiment (Figure 9). In the event, although only potassium bromide tracer could be used, the three tracer mass breakthrough curves for the three sections of the experiments were similar, with only a small increase in mass flux from the second section relative to the first, whereas the third section at the lowest application rate shows a tendency

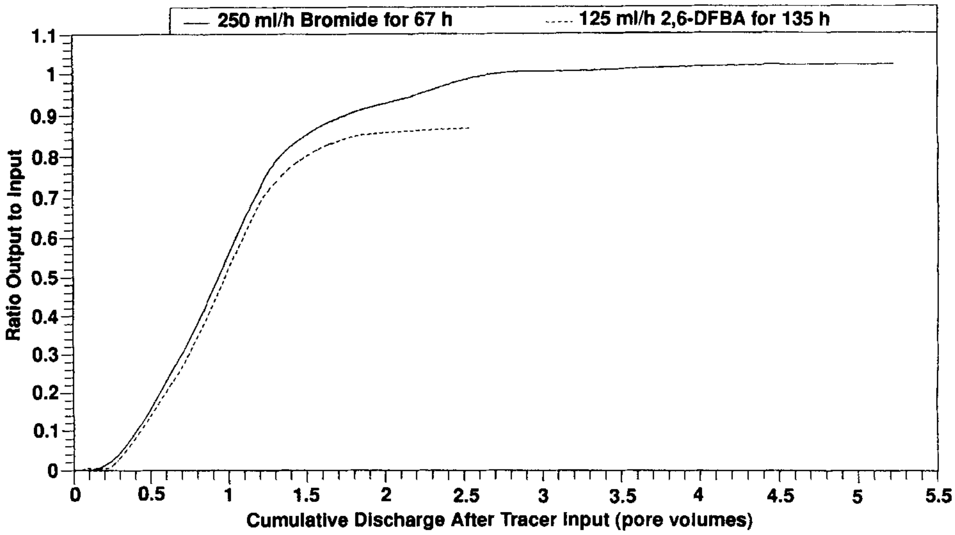

Figure 8. Breakthrough curves for bromide 2,6-DFBA for the steady-state rainfall experiment on the Slapton pasure soil core (SLG)

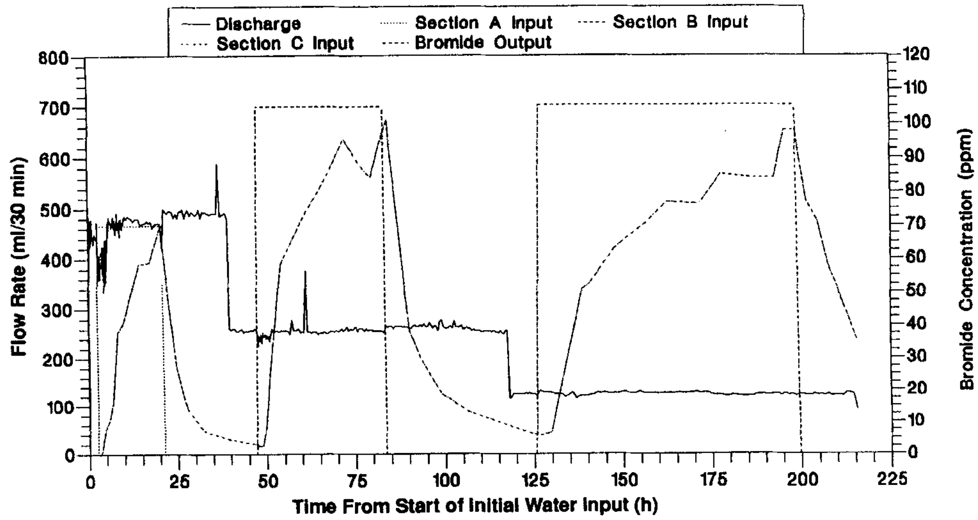

Figure 9. Discharge flow-rate and bromide input and output concentrations for each section of the steady-state return flow experiment on the Slapton woodland soil core (SLW)

for delayed and lower mass output relative to the first section (Figure 10). Separation of the discharge into bromide labelled water and unlabelled water follows the same pattern as the tracer output concentrations in Figure 9. Initial breakthroughs were again very rapid, 0·5 h (0·027 pore volumes) for the highest application rate, 1·83 h (0·05 pore volumes) for section SLW B and 2·0 h (0·027 pore volumes) for the lowest application rate. This core does not show the increase in effective porosity at breakthrough of the Slapton grassland core, suggesting perhaps that the preferential flow pathways in this woodland soil are structurally defined and less dynamic than the grassland column. On the other hand, the shape of the breakthrough curve suggests that a large proportion of the pore space is involved in the transport process. Maximum pore water velocities were 1·12, 0·30 and 0·28 ml h$^{-1}$ for the three sections of the experiment. A total of 82% of the tracer mass was recovered in section SLW A, 92% in section SLW B, whereas recovery in the last section was affected by leakage from the side of the column after the end of the tracer input.

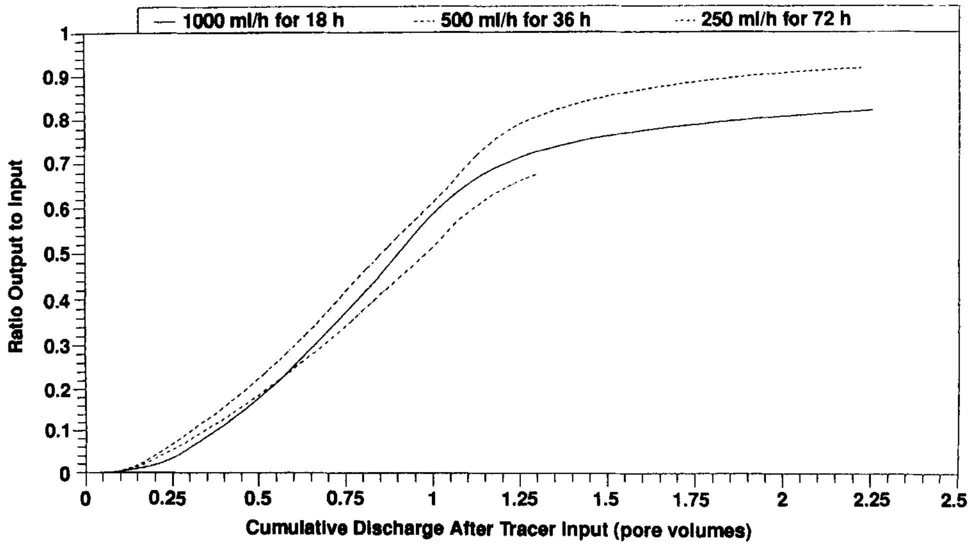

Figure 10. Breakthrough curves for the three tracer inputs of the steady-state return flow experiment on the Slapton woodland soil core (SLW)

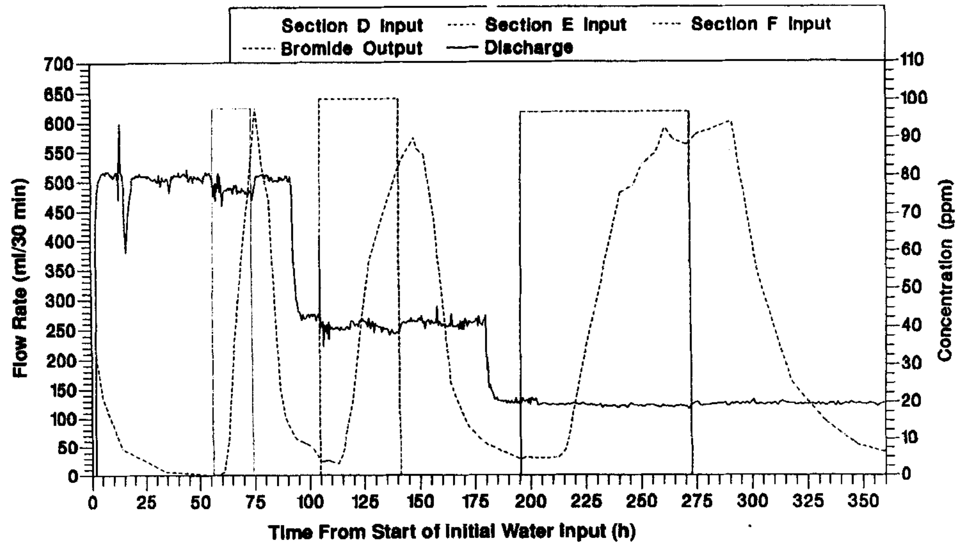

Figure 11. Discharge and tracer input and output concentrations during the steady-state rainfall experiment on the Slapton woodland soil core (SLW)

### *Steady-state rainfall flow experiment: Slapton woodland core SLW*

Figure 11 shows the discharges, input and output tracer concentrations from this set of experiments, whereas Figure 12 shows the cumulative mass breakthrough curves. Again all three sections of the experiment show broadly similar breakthroughs. The times to initial breakthrough were longer than for the return flow experiments, with correspondingly larger effective breakthrough pore volumes. Maximum pore water velocities were 0·224, 0·061 and 0·029 ml $h^{-1}$ for the three sections, much lower than for the return flow experiments. Again, this suggests that the upward flows are being locally channelled into distinct preferential flow pathways at the base of the soil, whereas the rainfall is subject to a more uniform infiltration distribution in the more open soil close to the surface. Mass recovery in each section was 92, 86 and 87% for the decreasing flow rates.

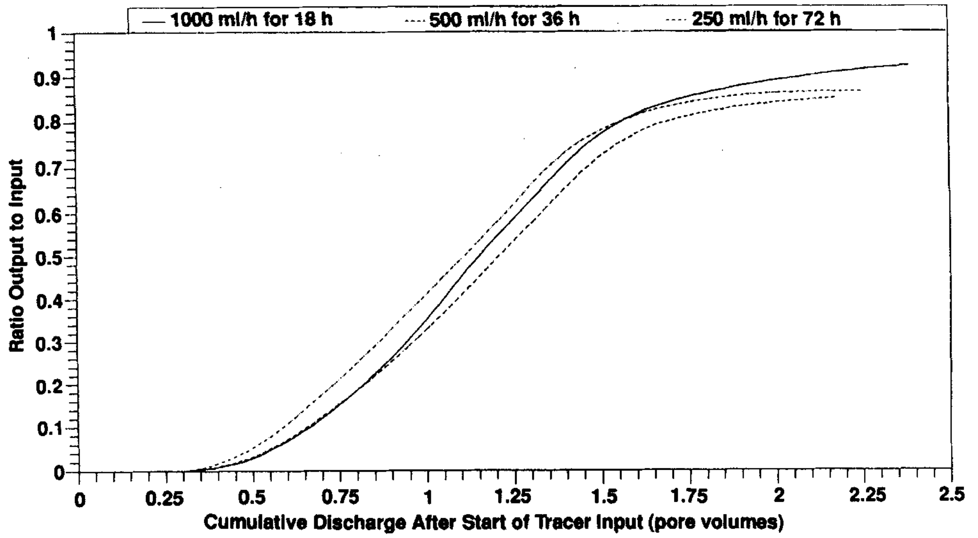

Figure 12. Breakthrough curves for the three tracer inputs of the steady-state rainfall experiment on the Slapton woodland soil core (SLW)

## DISPERSION PARAMETERS DERIVED FROM THE STEADY FLOW EXPERIMENTS

The results of steady state breakthrough curve (BTC) experiments are often analysed using the advection–dispersion equation (ADE), perhaps in a version that allows for exchange between mobile and immobile volumes or retardation of the tracer (see, for example, Parker and van Genuchten, 1984). The application of the ADE requires the calibration of, at least, a mean pore water velocity and a dispersion coefficient or dispersivity (or only the dispersion coefficient if the mean pore water velocity can be assumed known from the ratio of Darcian flux to average moisture content). More complex formulations might also require the calibration of the proportion of mobile pore water, an exchange coefficient, and a retardation coefficient. Beven *et al.* (1993) have provided a review of published values of dispersion parameters for experiments carried out on undisturbed soil cores. They showed that the experiments varied greatly in design, the scale of the cores used and the method by which the parameters were fitted. The range of published dispersion coefficient values is very high, spanning three orders of magnitude for undisturbed core experiments and four orders of magnitude in field plots.

In many of the experiments reviewed by Beven *et al.* (1993) the heterogeneity of flow pathways revealed by the tracer experiments suggests that the assumptions on which the ADE is based, in particular that

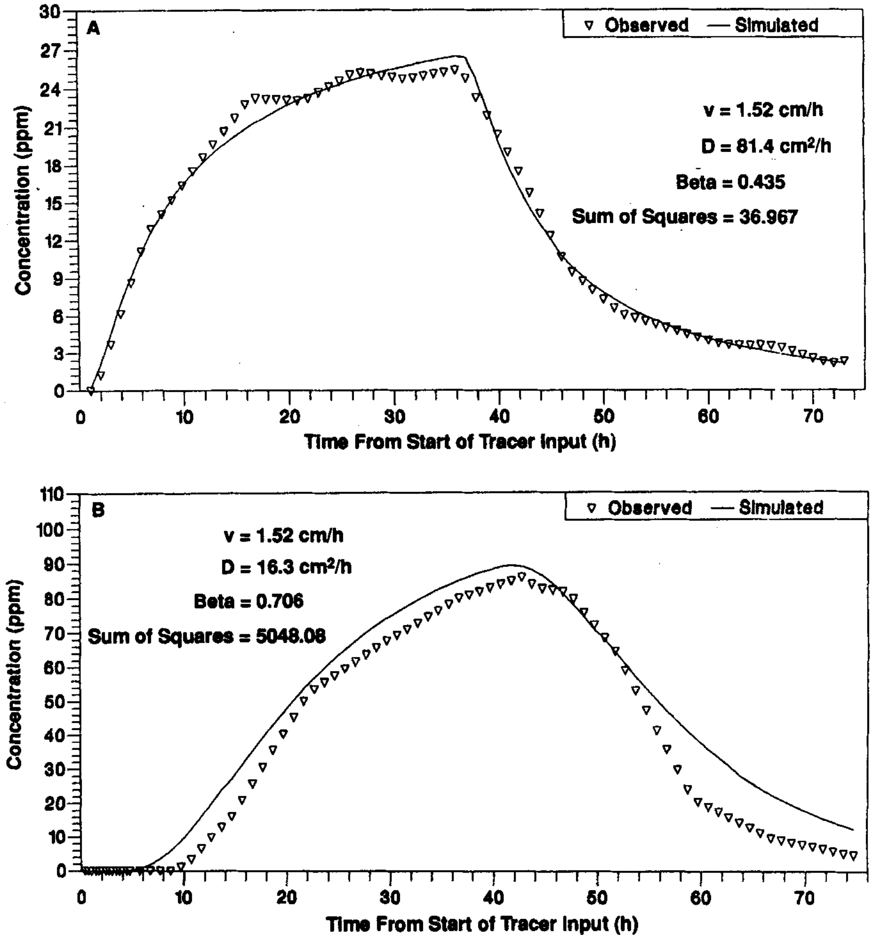

Figure 13. (A) Observed and simulated tracer concentration in discharge during section B of the steady-state return flow experiment on the Slapton pasture soil core (SLG). (B) Observed and simulated tracer concentration in discharge during section E of the steady-state rainfall experiment on the Slapton woodland soil core (SLW)

average concentrations and concentration gradients in the direction of flow can be defined, will not be valid. However, it is pointed out that the ADE can be used in a purely functional sense such that the mean transport velocity represents the mass flux of water averaged over some are of the system and the 'effective' dispersion coefficient reflects the complexities of the flow pathways and heterogeneities in local fluid velocities in the direction of flow, without any suggestion that the local mean concentrations or concentration gradients are measurable. The effective parameters may, however, be determined directly from measurements, such as the type of breakthrough measurements considered here. There are, however, some published data which cannot be modelled by a simple application of the ADE model (see, for example, Beven and Young, 1988).

In the case of the experiments reported here, the application of the ADE was reasonably successful, perhaps surprisingly given the rapid initial breakthroughs and high degree of bypassing inferred from the tracer measurements. The results of applying the ADE to the Lancaster and Slapton grassland cores (and some other Lancaster campus cores studied by Abdulkabir, unpublished data) were included in Beven *et al.* (1993, their table 2 and figure 1). Parameters were fitted using the CXTFIT package of Parker and van Genuchten (1984), which uses a non-linear least-squares optimization technique. There is a degree of uncertainty associated with these calibrated parameter values due to generally high degrees of intercorrelation among the parameters.

For the Slapton woodland core the application of the ADE to the measured breakthrough curves was also reasonably successful. In all cases, to reduce the dimensionality of the calibration problem, the mean pore water velocity was fixed at its estimated value (see tables mentioned earlier). In all the experiments for this core it was found that good fits could be obtained using only two additional parameters, the dispersion coefficient and the proportion of mobile pore water. It was not necessary to include a retardation coefficient or mobile/immobile water mixing coefficient. This was consistent with the results from other experiments.

The version of the ADE used is then defined by

$$\frac{\partial(\theta_m c_m)}{\partial t} = \frac{\partial}{\partial z}\left(\frac{\partial(\theta_m D c_m)}{\partial z}\right) - \frac{\partial(\nu \theta_m c_m)}{\partial z}$$

Where $c_m$ is the concentration of tracer in the mobile pore water, $\theta_m$ is the mobile pore water content, $v$ is

Table II. Calibrated dispersion parameters for the LUW2, SLG and SLW cores

| Experiment | Mean pore water velocity ($\mathrm{cm\,h^{-1}}$) | Dispersion coefficient ($\mathrm{cm^2\,h^{-1}}$) | Dispersivity (cm) | Proportion mobile water | Correlation coefficient ($R^2$) |
|---|---|---|---|---|---|
| Return flow | | | | | |
| LUW2A | 3·22 | 248·6 | 77·2 | 0·52 | 0·986 |
| LUW2B | 1·62 | 54·2 | 33·5 | 0·95 | 0·974 |
| LUW2C | 0·77 | 18·6 | 24·2 | 1·00 | 0·953 |
| SLG A | 3·04 | 370·0 | 121·7 | 0·61 | 0·970 |
| SLG B | 1·52 | 31·5 | 20·7 | 0·44 | 0·995 |
| SLG C | 0·76 | 15·5 | 20·4 | 0·33 | 0·967 |
| SLW A | 3·04 | 104·8 | 34·47 | 0·48 | 0·950 |
| SLW B | 1·52 | 127·8 | 84·1 | 0·47 | 0·981 |
| SLW C | 0·76 | 144·4 | 190·0 | 1·00 | 0·978 |
| Rainfall | | | | | |
| SLG D | 0·78 | 13·5 | 17·3 | 0·42 | 0·983 |
| SLG E | 0·41 | 8·4 | 20·5 | 0·47 | 0·967 |
| SLW D | 3·04 | 21·1 | 6·94 | 0·71 | 0·977 |
| SLW E | 1·52 | 16·3 | 10·72 | 0·71 | 0·940 |
| SLW F | 0·76 | 6·5 | 8·55 | 0·57 | 0·965 |

the mean pore water velocity, $D(-\alpha v)$ is the dispersion coefficient, $\alpha$ is the dispersivity, $t$ is time and $z$ is vertical distance.

Example measured and fitted dispersion curves are shown in Figure 13, including both the best fit (Figure 13A, $R^2 = 0{\cdot}994$) and worst fit (Figure 13*b*, $R^2 = 0{\cdot}940$) curves. A high degree of intercorrelation between the fitted parameter values was found again. The dispersion parameters for all the experiments are summarized in Table II.

For the rainfall experiments it was possible to use higher application rates with the Slapton woodland core. The results for the same rate as the Slapton grassland core show lower dispersion coefficients and dispersivities but a higher mobile water content. At the higher application rates the dispersivity stays at the same order of magnitude but there is an increase in the mobile water content.

Direct comparisons between rainfalls and return flows were possible for the Slapton woodland core (SLW). For the return flow experiments both dispersion coefficients and dispersivities were consistently high, and consistently higher than for the rainfall experiments at the same flow-rates. The proportion of mobile water content was lower than for the equivalent rainfall experiment for the two highest flow-rates, but then showed a significant increase (to 1·0) at the lowest flow-rate. The dispersive behaviour of this core appears to be different from either the Slapton grassland or Lancaster cores. In both of those cores dispersivity tends to decrease with decreasing flow-rate; for the woodland core there is a dramatic increase with decreasing flow rate. This inverse relationship is unusual in comparison with other changes in dispersivity with the flow rate reported previously.

It is worth noting that the values of dispersivity for the return flow experiments are significantly greater than the length of the core, suggesting that, particularly for the return flow experiments, the core scale is less than the mixing length for transport. This is consistent with the demonstrated importance of preferential flow in the columns. The dispersivities for rainfall are much less, suggesting more effective mixing for downwards flow. This difference is due to the smaller number of preferential flow pathways to be expected at the base of the column leading to a greater local differentiation in return flow transport than for rainfalls penetrating the more permeable soil near the soil surface.

Using the ADE in this way as a functional representation of the transport process in heterogeneous structured soil means that physical interpretation of calibrated parameter values must be limited. The results of these analyses serve to emphasise the very complex nature of transport processes in field soil, with effective parameters that vary with flow conditions and probably with the sequence of wetting and drying as flow pathways change. It is clear that the effective parameter values must be considered as very crude estimates of the field scale values needed for practical predictions. One methodology for the use of such single measurements to estimate field scale effective values, while taking account of the inherent uncertainty, is demonstrated in Beven (1993).

## SUMMARY

This work has examined transport and mixing processes in three large undisturbed soil cores using multiple tracer techniques. The need to check the suitability of the fluorobenzoate tracers before application is reinforced by the Slapton woodland core where only a bromide tracer could be used. Recovery from each experiment, even in this case, was such that it was possible to derive apparent dispersion parameters for each section of the experiments. It was found that the ADE modified to allow a proportion of immobile pore volume could be fitted to all the experimental tracer breakthrough curves using only two parameters, the dispersion coefficient and the proportion of mobile volume. It was not necessary to invoke either the retardation coefficient or the mobile–immobile mixing coefficient, thereby facilitating the calibration process, although it was found that the two fitted parameters were still strongly intercorrelated. Reducing the effective mobile pore volume in this case simply has the effect of changing the mean pore water velocity. Dispersion coefficients and dispersivities were considerably higher for the return flow experiments relative to rainfall experiments. This suggests that return flows are channelled into local preferential flow pathways at the base of the profile, thereby increasing the potential for bypassing flow higher in the column. This conclusion was reinforced by maximum pore water velocities at tracer breakthrough which again were much higher for return flows and by the final destructive sampling of the LUW2 core after a return flow experiment reported by Beven *et al.* (1993).

Calibrated effective dispersion coefficients and dispersivities generally decreased with increasing flow rate, but the Slapton woodland core was an exception in this respect. The calibrated proportion of mobile pore water tended to decrease with increasing flow-rate, but in this case the Slapton grassland core was an exception showing a significant increase. The results show that dispersion in undisturbed soil columns may be very difficult to predict. Neither dispersivities not mobile pore volumes are consistent, and both depend markedly on direction of flow, even under these near-saturated conditions.

Recovery of tracer from each section of the experiment ranged from 80 to more than 90%, but in every case there was significant retention of tracer in the column, with little evidence that this tracer is displaced rapidly by later additions of tracer. In one case, the use of the multiple tracers allowed the continued discharge of a bromide tracer to be distinguished for 5·2 pore volumes of flow through the column, at which point 15% of the added bromide remained retained in the column. It has been argued that much of this retention is due to physical mechanisms, including dispersion into relatively immobile flow pathways and diffusive mixing with water in immobile storage. It appears that this solute will be released from the column only over considerable periods of time. Similar retention and complex mixing processes have been inferred at the catchment scale for naturally occurring chloride by Neal *et al* (1988).

It therefore appears that these results have important implications for the interpretation of geochemical measurements, including solutes such as chloride which are often considered to be relatively conservative, and the modelling of solute transport in structured soil. At present, it appears to be difficult to make sense of fitted dispersion parameters while acknowledging the comparative similarity of the scaled breakthrough curves for different flow rates shown in Figures 2, 5, 8, 10 and 12. These suggest that, if they are treated as simple volume-weighted transfer functions, it may be possible to extrapolate behaviour from one flow-rate to another, an argument that has been made previously in the transient application of the Jury transfer function or stochastic–convection model (Jury and Roth, 1990; see Butters and Jury, 1989, and Roth *et al.*, 1991 for differing conclusions regarding the effectiveness of this model in applications to field tracer experiments). Prediction of solute transport remains problematic; the use of tracer experiments (and ideally multiple tracers) will consequently remain essential for the foreseeable future. The implications of the multicomponent tracer results for the modelling and prediction of transport in soils is discussed further in Part 3 of this series.

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## REFERENCES

Beven, K. J. 1993, 'Estimating transport parameters at the grid scale: on the value of a single measurement', *J. Hydrol.*, **143**, 109–123.

Beven, K. J. and Young, P. C. 1988. 'An aggregated mixing zone model of solute transport through porous media', *J. Contaminant Hydrol.*, **3**, 129–143.

Beven, K. J., Henderson, D. E. and Reeves, A. D. 1993. 'Dispersion parameters for undisturbed partially saturated soil', *J. Hydrol.*, **143**, 19–43.

Bowman, R. S. 1984. 'Evaluation of some new tracers for soil water studies', *Soil Sci. Soc. Am. J.*, **48**, 987–993.

Butters, G. L. and Jury, W. A. 1989. 'Field scale transport of bromide in an unsaturated soil, 2. Dispersion modelling', *Wat. Resour. Res.*, **25**, 1583–1589.

Jury, W. A. and Roth, K. 1990. *Transfer Functions and Solute Movement Through Soil: Theory and Applications*. Birkäuser, Basle. 239pp.

Levy, B. S. and Germann, P. F. 1988. 'Kinematic wave approximation to solute transport along preferred flow paths in soils', *J. Contam. Hydrol.*, **3**, 263–276.

Neal, C., Christophersen, N., Neale, R., Smith, C. J., Whitehead, P. G. and Reynolds, B., 1988. 'Chloride in precipitation and streamwater for the upland catchment of the River Severn, mid-Wales; some consequences for hydrochemical models', *Hydrol. Process.*, **2**, 155–166.

Parker, J. S. and van Genuchten, M. Th. 1984. 'Determining solute transport parameters from laboratory and field tracer experiments', *Va. Agric. Exp. Stn. Bull.*, **84-3,** 96pp.

Roth, K., Jury, W. A., Flühler, H. and Attinger, W. 1991. 'Transport of chloride through an unsaturated field soil', *Wat. Resour. Res.*, **27**, 2533–2541.