Following tracer through the unsaturated zone using a multiple interacting pathways model: Implications from laboratory experiments

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Abstract
Models must effectively represent velocities and celerities if they are to address the old water paradox. Celerity information is recorded indirectly in hydrograph observations, whereas velocity information is more difficult to measure and simulate effectively, requiring additional assumptions and parameters. Velocity information can be obtained from tracer experiments, but we often lack information on the influence of soil properties on tracer mobility. This study features a combined experimental and modelling approach geared towards the evaluation of different structures in the multiple interacting pathways (MIPs) model and validates the representation of velocities with laboratory tracer experiments using an undisturbed soil column. Results indicate that the soil microstructure was modified during the experiment. Soil water velocities were represented using MIPs, testing how the (a) shape of the velocity distribution, (b) transition probability matrices (TPMs), (c) presence of immobile storage, and (d) nonstationary field capacity influence the model's performance. In MIPs, the TPM controls exchanges of water between pathways. In our experiment, MIPs were able to provide a good representation of the pattern of outflow. The results show that the connectedness of the faster pathways is important for controlling the percolation of water and tracer through the soil. The best model performance was obtained with the inclusion of immobile storage, but simulations were poor under the assumption of stationary parameters. The entire experiment was adequately simulated once a time-variable field capacity parameter was introduced, supporting the need for including the effects of soil microstructure changes observed during the experiment.

KEYWORDS
celerity, soil properties, tracer mobility, velocity
1 | INTRODUCTION

Tracer velocities, a measure of how quickly pore water moves through the soil profile, are different from celerities, which are a measure of how quickly flow rates of water respond to a rainfall event (Beven, 1989, 2012). Differences between velocities and celerities are thought to explain the rapid run-off of stored water during rainfall events (McDonnell & Beven, 2014) and therefore provide an explanation for the old water paradox (Beven, 1989; Kirchner, 2003; McDonnell, 1990).

Flow and transport networks in soils are controlled by cycles of wetting and drying; freezing and thawing; shrinking and swelling; organic matter accumulation and decomposition; biological activities; and chemical reactions that ultimately generate soil aggregates and pore networks (Jarvis, 2016; Lin, 2010). The term “preferential flow” encompasses all the processes that occur in non-uniform soils where part of the flow through the soil bypasses parts of the matrix (Beven & Germann, 1982, 2013; Jarvis, 2016; Beven, 2018). Eventually, the ways in which the occurrence and characteristics of preferential flow influence the infiltration of water and solutes through the soil are still not well understood.

Time-variant transit-time distributions and novel modelling techniques attempt to represent the effects of this velocity/celerity interplay (Laine-Kaulio, Backnäs, Karvonen, Koivusalo, & McDonnell, 2014; Rinaldo et al., 2011; Scedeler et al., 2016; Soulsby et al., 2015) but are often focused at hillslope and catchment scales. Thus, they are unable to directly address the role of soil structure on subsurface velocities. Particle tracking techniques instead are able to include velocity distributions explicitly in the modelling domain (Davies, Beven, Nyberg, & Rodhe, 2011; Davies, Beven, Rodhe, Nyberg, & Bishop, 2013; Henri & Fernández-Garcia, 2014; Maier & Bürger, 2013; Tschiesche, 2012; Zehe & Jackisch, 2016).

However, few studies have analysed in situ velocities and celerities to test the interplay between these variables (Beven & Davies, 2015; Mosley, 1982; Öztürk & Özkan, 2002; Scaini et al., 2017, 2018). Although soil structure is expected to control subsurface flowpaths and hydraulic response, how that structure relates to velocity distributions, including preferential flows, remains poorly understood (Beven, 2018; Beven & Germann, 2013). Here, we seek to assess the influence of soil structure on water velocities, as inferred from a particle tracking model—the multiple interacting pathways (MIPs) model.

MIPs are a particle tracking model developed to predict both hydrographs and tracer breakthrough curves (Beven, Hornberger, & Germann, 1989). The MIPs model has been used in theoretical studies to explore the influence of velocity distributions on flow and transport (Davies & Beven, 2012), as well as scale and hysteresis effects (Davies & Beven, 2015). MIPs has been applied at hillslope (Davies et al., 2011) and catchment scale (Davies et al., 2013) and tested using discharge, water table, and geochemical and isotopic data using a hypothesis-testing approach.

MIPs allow inclusion of transition probability matrices (TPMs), which control exchanges between flow pathways of different velocities and therefore simulate the effects of capillarity, connectivivity, and preferential processes (Davies et al., 2011), noting that any effects of capillarity will be small under the conditions of the experiment. The MIPs hillslope scale application reproduced discharge and tracer breakthrough well after making some assumptions regarding tracer release and boundary conditions. The catchment scale study showed that simulating some exchange between pathways using the TPMs was important for testing a behavioural hypothesis.

Previous MIPs applications hint at the importance of velocity distributions and TPMs as mechanisms for characterizing the flow domain and assessing the power of models and experiments that consider both velocity and celerity for testing hypotheses and getting the right answers for the right reasons (Beven, 2018; Kirchner, 2006). However, the model has only been applied at hillslope and small catchment scale in one location, and exploration of how the choice of velocity distributions and TPMs influence the flow and transport response remained limited in the earlier papers.

Conservative tracer experiments can be simulated in MIPs to explore, through different representations of velocity distributions and TPMs, the occurrence and characteristics of preferential flow processes. In order to test the MIPs framework properly, both fluxes and transport information are required. For most studied catchments, there is usually some information available on celerity, as celerity information is implicit in water table, hydrograph, and rainfall–run-off responses.

Tracers offer a tool to characterize integrated Lagrangian water velocities and pathways (McGuire & McDonnell, 2015; Trudgill, Pickles, & Smettem, 1983). In particular, salt tracers are widely used both at field and laboratory scales due to their high availability, solubility, and low cost (Flury & Papritz, 1993; Hornberger, Germann, & Beven, 1991; Mortensen, Jensen, Nilsson, & Juhler, 2004). The interpretation of tracer concentrations in time, the tracer breakthrough curve, is complicated by the frequency of observations in time and space as well as analysis techniques (Abbott et al., 2016; Weihermüller et al., 2007). Moreover, tracers are often nonconservative, due to the many processes that can influence tracer movement in the soil: precipitation and deposition processes, anion exclusion, and anion retardation phenomena (Flury & Wai, 2003), as well as sorption processes caused by the positive charge of the soil (Sposito, 1989). Due to these phenomena, the addition of salts to soils often leads to changes in soil microstructure (Durst, Imfeld, & Lange, 2013).

Here, we investigate celerity and velocity at a smaller scale by relying on a combined laboratory–modelling experimental approach. We conduct a structurally intact column experiment and apply a 1-D version of the MIPs model, testing hypotheses with regard to (a) the velocity distribution in the soil column, (b) the TPMs, (c) the presence of immobile water, and (d) nonstationary field capacity (FC). To do so, we describe the study site and soil properties (Section 2) and the column experiment (Section 3). The experiment results (Section 4) provide the basis for refining hypotheses aimed at reproducing the experiment within the MIPs model conceptualization (Section 5). The output from the application of the model (Section 6) allows a discussion of inferred soil properties (Section 7). The main findings are described in Section 8.
The soil material used in this study comes from the Weierbach, an experimental forested catchment located in the north-west of Luxembourg, underlain by Devonian slate. Elevation ranges from 422 to 512 m a.s.l. The Weierbach catchment has been monitored for its hydroclimatic response for more than 20 years.

The soil is classified as a Dystric Cambisol (Ruptic, Endoskeletic, Siltic, and Protosodic) in the World Reference Base for Soil Resources (IUSS Working Group, 2015) and is divided into an upper thin organic rich Ah horizon (0- to 5-cm depth) and a cambic Bw horizon (5- to 50-cm depth), developed on a loamy material that originated from periglacial atmospheric deposits (Figure 1). The 2C horizon mixes periglacial deposits and slate bedrock residual clasts. The slate clasts increase significantly with depth, from 15% to 50% v/v. The deeper rocky substratum, from 90 cm to a variable depth averaging about 500-cm depth, is constituted by a weathered and fractured slate. Previous hydrological investigations have shown that mean porosity decreases from the soil surface to the fresh bedrock: 75%, 65%, and <9% for the A, B, and C horizons, respectively (Martínez-Carreras et al., 2016).

Table 1 shows the characteristics and initial conditions of the undisturbed soil column used in this study, taken from the soil analysis of Martínez-Carreras et al. (2016). Soil properties were characterized using soil core data information from site 5 in Martínez-Carreras et al. (2016), the sampling site where the soil and column were extracted. All physical parameters correspond to the average value calculated using six replicates of undisturbed soil cores (100 cm³) sampled for each soil horizon (Table 1). Bulk density was determined by the ratio between the soil dry weight (soil dried at 105°C for 48 hr) and the ring volume of the soil core sampler. Hydraulic conductivity at saturation ($K_s$), total porosity ($\theta_s$), based on the standard relationship between bulk density and particle density, field capacity (i.e., the total water content in a soil that has been drained by gravity) determined as the average soil moisture content at 60 mbar (pF 1.8), with a coefficient of variation between 1% and 5% for the layers Ah and Bw. These ranges were employed as allowed parameter ranges for the undisturbed soil column characterization in multiple interacting pathways. Error estimates refer to one standard deviation.

In the Weierbach catchment, $\theta_s$ estimates were rather constant with depth in the first metre of soil depth (Martínez-Carreras et al., 2016).

### Table 1

| Soil properties | Ah     | Bw     |
|-----------------|--------|--------|
| Bulk density, g m⁻³ | 0.64 ± 0.10 | 0.87 ± 0.05 |
| Estimated total porosity ($\theta_s$), m³ m⁻³ | 0.75 ± 0.03 | 0.67 ± 0.02 |
| Saturated hydraulic conductivity ($K_s$), m day⁻¹ | 11.21 ± 10.37 | 16.31 ± 10.03 |
| Soil at field capacity, m³ m⁻³ | 0.41 ± 0.05 | 0.37 ± 0.02 |

Note. Bulk density was determined by the ratio between the soil dry weight (soil dried at 105°C for 48 hr) and the ring volume of the soil core sampler. Hydraulic conductivity at saturation ($K_s$), total porosity ($\theta_s$), based on the standard relationship between bulk density and particle density, field capacity (i.e., the total water content in a soil that has been drained by gravity) determined as the average soil moisture content at 60 mbar (pF 1.8), with a coefficient of variation between 1% and 5% for the layers Ah and Bw. These ranges were employed as allowed parameter ranges for the undisturbed soil column characterization in multiple interacting pathways. Error estimates refer to one standard deviation.

## 3 | UNDISTURBED COLUMN EXPERIMENT

A 25 × 25 × 25 cm size undisturbed soil column was extracted from the field site, in the vicinity of location 5 in Martínez-Carreras et al. (2016), using the protocol described by Bagarello and Sgroi (2008).
3.1 Experiment set-up

The pore volume of the column, defined as the volume of pores that can be filled by water, was calculated using the porosity information calculated on both horizons Ah and Bw on the core samples of Section 2, expressed as total porosity—obtained by multiplying the core volume by the estimated porosity (Reeves, Henderson, & Beven, 1996). Tracing experiments were carried out using NaCl as a tracer in concentration of 1 g L\(^{-1}\). During the column experiment, a total of 12 L (1.09 pore volume) was applied on the surface of the soil column.

The column experiment was performed over 3 days in a greenhouse located at the Luxembourg Institute of Science and Technology in Luxembourg. The phases of the experiment are shown in Table 2. On the first day (Event 1), the column was submerged in water from the Weierbach creek to totally saturate the soil porosity and was laid on a plastic support until reaching FC (i.e., until the outflow collected from the bottom of the column was negligible). To support the column during the experiments, the top surface of the plastic support was left open to infiltration, and the bottom surface was left open for drainage. Consequently, 1 L of water (from the Weierbach catchment) was applied to wet-up and rinse the column. The water input was applied from above onto the surface of the column. More water was applied only after the previous application had completely infiltrated. After the applied water completely infiltrated into the surface, 2 L of tracer solution with a concentration of NaCl of 1 g L\(^{-1}\) was applied. Once the water had percolated, the rinsing phase started (elapsed times in minutes are shown in Table 2). A total of 9 L was used to rinse the column—2 L on the same day, followed by 5 L, divided into two events separated by 6 hr (Events 2 and 3), and 2 L (Event 4) over the following 2 days (Table 2).

### TABLE 2 Characteristics of the tracer application and rinsing events during the column experiment

| Time | Event n | Phase       | Applied water (L) | Equivalent PV | Time between previous and current phase (min) | Time to outflow (min) |
|------|---------|-------------|-------------------|----------------|-----------------------------------------------|----------------------|
| Day 1 | Event 1 | Water       | 1                 | 0.09           | 0.5                                           |                      |
|      |         | NaCl solution | 2                 | 0.18           | 20                                            | 1.2                  |
|      |         | Rinsing     | 2                 | 0.18           | 5                                             | 1.5                  |
| Day 2 | Event 2 | Rinsing     | 4                 | 0.36           | 570                                           | 1.3                  |
|      | Event 3 | Rinsing     | 1                 | 0.09           | 360                                           | 1.4                  |
| Day 3 | Event 4 | Rinsing     | 2                 | 0.18           | 1080                                          | 1.7                  |

Note. Both the applied water, expressed in litres, and the equivalent pore volumes (equivalent PV) are provided. For each phase, the time between the end of the previous phase and the beginning of water application of the current phase is shown. Additionally, the time it took for water to percolate through the column (i.e., to the start of outflow), expressed in minutes, is also shown.

Abbreviation: PV, pore volume.

3.2 Output measurements

Outflow volumes were measured by weighing samples collected every 5 min. For each event, discharge ratios were calculated by dividing the water inflow by the water outflow. Tracer concentrations were measured at variable time steps, between 5 and 20 min. The water samples were filtered using Acrodisc syringe 0.45-μm filters (Pall Corporation) and analysed for chloride (Cl\(^-\)) concentrations using ionic chromatography ( Dionex ICS-5000). Cl\(^-\) detection limit was 0.01 mg L\(^{-1}\).

Cl\(^-\) output concentrations were used to calculate the mass of Cl\(^-\) leaving the system. As not all samples were analysed, the mass of Cl\(^-\) was estimated by (a) interpolating linearly between the measured points to match the sample timing of the outflow volume, (b) multiplying Cl\(^-\) concentrations to outflow volume to obtain the load, and (c) summing up all the values to obtain the total mass of Cl\(^-\).

4 EXPERIMENTAL RESULTS

4.1 Column experiment results

Because the water application rate at the column surface exceeded the infiltration rate, ponding was observed at the initial stages of all the water application events. The total volume measured for Cl\(^-\) concentration was 7 L. With the use of the interpolation technique described in Section 3, a recovery of 78% in Cl\(^-\) was estimated, showing that about one pore volume was sufficient to rinse out a large part of the applied tracer.

The analysis of the experimental results proved challenging given that the column experiment for Event 1 held more water (as determined from the volume of outflow) than for Events 2 and 3, where outflow was larger than input. Although the total mass balance between the input volume and the retrieved volume suggested an almost complete recovery, reaching 97%, the mass balance for each individual event did not add up, as shown in Table 3.

4.2 Model hypotheses to be tested

The mismatch between inflow and outflow volumes suggested two possibilities:

1. Experimental error, due to unaccounted evapotranspiration losses. This possibility was ruled out, on the grounds of low values of

### TABLE 3 Inflow/outflow rate, expressed in %, for each event during the experiment

| Time | Event n | Inflow | Outflow | Outflow/inflow (%) |
|------|---------|--------|---------|-------------------|
| Day 1 | Event 1 | 5      | 4.2     | 84                |
| Day 2 | Event 2 | 4      | 4.1     | 103               |
|      | Event 3 | 1      | 1.5     | 150               |
| Day 3 | Event 4 | 2      | 1.8     | 90                |
| Total |         | 12     | 11.6    | 97                |
estimated actual evapotranspiration (up to 1 mm day$^{-1}$) at the experiment location, which would be enough to explain up to approximately 50% of the mismatch but not all of it.

2. Modified pore structure or variable moisture conditions causing a variable volume of immobile water storage. At this site, a structural change following a multitracer experiment performed at field scale was suggested by the work of Scaini et al. (2017). This possibility was supported by previous studies showing the significant dependence of FC on moisture conditions (e.g., Kampf, 2011).

On the basis of this result, we present hereafter a 1-D version of the MIPs model that incorporates the experimental knowledge gained with the column experiment. We use the model to explore the various possibilities that could explain the structural change observed both in field and column experiments (Figure 2). The model was run using the data from the undisturbed column experiment to test which process representation hypothesis can best reproduce the experimental observations.

We tested the following model hypotheses:

H1. Both discharge and tracer outputs are affected by the shape of the velocity distribution.

H2. Pore connectivity, conceptualized here with TPMs, can affect water and tracer retention.

H3. Water storage can be treated as effectively immobile when it falls below FC (FCH3), to enhance the retention of tracer in the soil.

All hypotheses were tested while keeping the soil characteristics ($\theta$ and $K_s$) within measurement limits, set by the available measurements described in Section 2.

The variable discharge ratios observed (Table 3) suggested that it would be necessary to allow changes of soil properties in time, as suggested by previous field experiments, where the addition of NaCl applied in concentration of 5 g L$^{-1}$ causes a decrease in infiltrability (Scaini et al., 2017). To address this, an additional hypothesis was tested that allowed adjusting soil characteristics outside the measurement bounds of Table 1:

H4. Changes in water storage can be characterized by a time-variable FC parameter (FCH4) to reflect microstructure changes.

5 | MULTIPLE INTERACTING PATHWAYS FORMULATION

5.1 | Modelling conceptualization and requirements

We used a 1-D MIPs model, with velocities driven by gravity, representing the free-draining column, and able to account for the ponding at the surface of the column in case precipitation exceeded infiltration rates. Such an approach is consistent with the type of Stoke's flow representation of water movement under gravity as suggested by Germann (2018) and Beven and Germann (2013). MIPs represent water within the soil system as a large number of
representative particles, which move through the system with velocities randomly selected from a predefined velocity distribution. Each particle represents part of the soil water moving with that chosen velocity but may be spread across the pore space (here, the particle volume equals 1 ml). The position, velocity, and chemical composition (here, Cl\(^-\) concentration) of the particles can be tracked and stored at each time step (here, time step length is 5 min).

In the original MIPs model (Davies et al., 2011, 2013), given an infiltration rate, the water particles were assigned an exponential velocity distribution, which was partly dependent on the moisture content that would be reached through that infiltration rate, if applied continuously. Here, this assumption was kept only for the newly added particles, whereas for the pre-existing particles in the unsaturated zone, the velocities were dependent on water content in the vicinity of each particle, which was calculated using layers of 1 cm at each time step (Equation 1).

\[
v = v_0 \cdot \exp(b \cdot \theta - R)
\]

where \(v_0\) [m \cdot d\(^{-1}\)] is the minimum pore-water velocity; \(b [-]\) is a parameter defining the skewness of the distribution; \(\theta\) [m\(^2\) \cdot m\(^{-3}\)] is the volumetric water content in the layer, ranging between 0 and porosity \(\theta_s\); and \(R [-]\) is a vector with uniform random distribution and length equal to the number of particles in each layer.

For the time steps when infiltration was greater than zero, the velocity distribution of the newly added particles was defined again as in Equation (1), but this time, \(\theta\) was the water content that would be reached under a steady state with the given infiltration rate applied, and \(R\) was a vector with uniform random distribution and length equal to the number of particles added at a given time step. Ponding at the soil surface was regarded as surface storage, which infiltrated gradually through the column.

At each time step, the water content \(\theta\) of each layer was calculated and used to produce the velocity distribution within that layer. The integral of unit gradient velocities equals the vertical hydraulic conductivity \(K\) (Equation 2).

\[
K = \int_0^\theta v \cdot d\theta
\]

Porosity \(\theta_s\) can be derived as a function of saturated hydraulic conductivity \(K_s\), \(v_0\), and \(b\), combining Equations (1) and (2). For each model run, aiming at keeping \(\theta_s\) and \(K_s\) within the measurement range, two combinations of parameters \(v_0\) and \(b\) were used. First, \(v_0\) was assigned two arbitrary values (0.1 and 1 cm day\(^{-1}\)). The parameter \(b\) was then derived (17.9 and 14, respectively), as a result of manual calibration of the modelled versus measured cumulative discharge and tracer export. The first set of parameters resulted in high skewness of the velocity distribution and will be referred here below as \(S_{K+b}\). The second set of parameters, with lower skewness, will be referred to as \(S_{K-L}\).

In all model versions that were set up for the hypothesis testing, the initial moisture content was set within the limits of FC as determined in Section 2. When the column surface was ponded, the full velocity distribution equivalent to \(K_s\) (as in Equation 2) was used. For inputs of tracer solution, each input particle was labelled with the corresponding tracer concentration.

To examine the effect of pore-water velocity distribution on discharge and tracer transport (i.e., H1), the model was run with the two velocity distributions described above. The hypotheses regarding the soil microstructure and pore connectivity, H2, were examined by employing the TPM and comparing the modelled and measured Cl\(^-\) mass outputs. The role of the TPM was to control how the water particles exchange their velocities while they travel through the soil. For the cases where a TPM was not specified, each particle was assigned a new velocity at every time step, randomly selected from the velocity distribution described in Equation (1). This set-up will be called the high exchange scenario (ExH) and can be described as fast exchange between flowpaths, representing a structure where the spatial correlation of the pore size is very small. When TPM was specified, the probability to exchange velocity could be adjusted so that the water particles would selectively tend to retain their velocities. This case will be referred to as the low exchange scenario (ExL).

Scaini et al. (2017) suggested the high velocities observed at the plot scale to imply pore continuity (Yousefi et al., 2014). In the MIPs model, pore structure and continuity can be related back to different scenarios of water particle velocity exchange as expressed in the TPM. We assume that if a water particle was travelling along a macropore (and therefore had high velocity), (a) the probability for it to keep moving along this macropore and not infiltrate into smaller pores was high, and (b) the length of the pores was on average longer than what a particle could cover within a time step.

At each time step, all the particles of each layer were equally split in three velocity classes: slow, medium, and fast (i.e., one third of the particles of the layer was called slow, one third medium, and one third fast). The probabilities to change from one class to another (i.e., TPM) were set according to two rules: (a) the sum of probabilities for a particle to be found in any class during a time step is 100\% (i.e., the sum of each row and column of Table 4 is 100) and (b) the particles have a lower probability (20\% chance) to move to a different velocity class and a higher probability (80\% chance) to stay in the same velocity class (Table 4).

For all the cases of velocity distribution (H1) and velocity exchange probability (H2), initial modelling experiments showed that it was difficult to produce sufficient retention of tracer between successive applications, if no constraints on drainage were imposed. Allowing part of the pore space to remain immobile and exchange tracer with the mobile particles was considered but not tested, as this would require introducing additional parameters (e.g., location of immobile particles and exchange rate between immobile storage and mobile pathways). We tested a

| TABLE 4 | Probability (%) for a particle to move from a velocity class (shown in the left-most column) to another velocity class (shown in the top-most row) |
|---------|---------------------------------------------------------------|
| From    | Slow | Medium | Fast |
| Slow    | 80   | 10     | 10   |
| Medium  | 10   | 80     | 10   |
| Fast    | 10   | 10     | 80   |
simpler approach instead: Particles within a layer with soil moisture at FC (FC_{143}) were assigned zero velocity (H3). The particles regained a nonzero velocity, consistent with Equation (1) once the moisture content again exceeded FC_{143}. Restraining drainage at FC_{143} can be conceptually related to (a) low relative hydraulic conductivities (reflected in the velocity distribution) and (b) capillary gradients acting against gravity (which are not explicitly considered in MIPs). This approach produced satisfactory results with only one additional parameter, FC_{143}.

To test H4, a time-variable FC was introduced (FC_{143}). Here, it was assumed that the soil column FC was positively correlated to the soil moisture content. Consequently, at the beginning of each event, when the soil was relatively dry, the FC would be lower, and it would increase as the event water infiltrated the column. For each of the four events, FC_{143} was given two different values, ranging between 0.28 and 0.42. The values were adjusted through manual calibration of the model to measured discharge and Cl\(^{-}\) export. Furthermore, in H4, the values of K\(_s\) and porosity parameters were allowed to exceed their measurement limits (3.8 m day\(^{-1}\) and 68%, respectively).

### 5.2 Model evaluation

The modelled discharge and Cl\(^{-}\) outputs were evaluated in two different ways. First, a two sample Kolmogorov–Smirnov (K-S) test at 0.05 significance level was performed. The null hypothesis (h) was that the measured and modelled data series come from the same continuous distribution. Below, the cases where the null hypothesis was rejected are symbolized with h = 1, whereas failing to reject the null hypothesis is symbolized with h = 0.

For the discharge, measured and modelled cumulative discharge normalized to total input (Equation 3) were compared.

\[
Q_{c} = \sum_{i=1}^{N} Q(t) / \sum_{i=1}^{N} I(t), \quad t = 1, \ldots, N \tag{3}
\]

where I(t) is the input per time step and N is the total number of discharge measurements.

For the Cl\(^{-}\) export, the measured and modelled cumulative and normalized to total Cl\(^{-}\) input, corrected for the initial Cl\(^{-}\) content, was used (Equation 4).

\[
Cl_{c} = \frac{\sum_{i=1}^{N} Cl_{in}(t)}{\left(\sum_{i=1}^{N} Cl_{in}(t) + Cl_{i0}\right)}, \tag{4}
\]

where Cl\(_{in}\) is the Cl\(^{-}\) input (mg) at every time step and Cl\(_{i0}\) is the initial Cl\(^{-}\) content in the soil column.

The K-S test was used to evaluate if the compared data series came from the same continuous distribution. Modelled discharge and Cl\(^{-}\) outputs were also evaluated against measurements by calculating the coefficient of determination, R\(^2\) (Equation 5), noting that in using cumulative values, successive values are not independent.

\[
R^2 = 1 - \frac{\sum_{i=1}^{N} (Q_{c,\text{mod}} - Q_{c,\text{meas}})^2}{\sum_{i=1}^{N} (Q_{c,\text{meas}} - Q_{c,\text{meas}})^2}, \quad t = 1, \ldots, N. \tag{5}
\]

### 6 | MULTIPLE INTERACTING PATHWAYS

RESULTS

Figure 3 shows the simulation results for H1 and H2, where all the water was assumed to be mobile. The shape of cumulative normalized discharge (Figure 3a) was different for the two velocity exchange probability scenarios, during the first event (between 0 and 65 min). Although the drainage was gradual throughout the whole simulation period for the high exchange scenario (ExH, dashed lines), there was an abrupt draining at the beginning of the simulation for the low exchange scenario (ExL, solid lines). The scenario with higher velocity skewness (Sk, yellow) showed faster draining during this first event. The velocity distribution skewness made a greater difference when high velocity exchange was allowed. The responses of all the scenarios were similar for the following events (2, 3, and 4), and all of them retained more water comparing with the measurements. Although the measured data showed that 96% of the input water was drained after the end of the experiment, the four modelled scenarios predicted drainage between 72% and 76%.

The discharge and tracer export pattern during the first event for the ExL scenario pointed to a conceptual case where pre-existing water in the soil column was removed first, and there was maximal discharge through bypass flow. However, this is not in agreement with the experiment results (Figure 3).

Figure 4 shows the simulation results combined with the immobile component hypothesis, that is, H3. The introduction of FC overall improved the simulations of both discharge and tracer export (Table 5). The modelled volume performance across all the models tested had R\(^2\) ranging between .62 and .99 (Table 5). The tracer recovery was overestimated (88% vs. 78% of the measured) for all tested hypotheses (Figures 3b and 4b), and despite R\(^2\) ranging between .86 and .93, the dynamics of Cl\(^{-}\) export were not well represented with too little Cl\(^{-}\) being retained in the column over the full course of the experiments.

The results of the K-S test (at 0.05 significance level) are shown in Table 4. For all the tested cases (H1, H2, and H3), the null hypothesis was either rejected (h = 1, p < .05) or could not be rejected, but in these cases, the p value was much larger than .05 (h = 0, p > .05).

The tests with FC\(_{143}\) allowed to better reproduce the experiment, with R\(^2\) .98 and .97 for Q\(_c\) and Cl\(_c\), respectively (Figure 5). In this case, the results of the K-S test for Q\(_c\) were h = 0, p > .05, and for Cl\(_c\), h = 0, p > .05. Also, this was the only instance where the measured and modelled Cl\(^{-}\) export matched closely at the end of the experiment.

### 7 | DISCUSSION

Undisturbed soil column experiments are often used to analyse natural soil properties via responses to tracer addition. Even in such controlled conditions, analysing the changes in soil structure remains a challenge—despite the possibility for thin-sectioning the column (Bouma, Jongerius, Boersma, Jager, & Schoonderbeek, 1977) or performing 3-D imaging and X-ray tomography (Anderson, Peyton, & Gantzner, 1990; Garel et al., 2012; Luo, Lin, & Li, 2010; Wildenschild et al., 2002).
The observed shift in the response from Event 1 (the first day) and the other 2 days of rinsing the applied salt (Events 2, 3, and 4) suggested that there were changes to the pore structure and, consequently, the FC, during the experiment—as also observed in the field study of Scaini et al. (2017). This change occurred due to the application of 2 L of solution with a concentration of NaCl of 1 g L\(^{-1}\) (Section 3). Other studies have shown significant retention of tracer in undisturbed cores, despite the application of more than four to five pore volumes of water (Abdulkabir, Beven, & Reeves, 1996) and that hydraulic conductivity decreases in response to an increase of Cl\(^{-}\) concentration in laboratory conditions (Devrajani, 1993). In the absence of information on such complex processes, we tested different model hypotheses that could help explain the apparent changes in pore structure after the salt application. Below, we discuss the hypotheses tested with MIPs in order to better understand the observations.

### 7.1 The influence of the shape of the velocity distribution on discharge output (H1)

The concept that velocity and pore size are interconnected has been suggested before (Beven & Germann, 1981; Germann & Beven, 1981; Siena, Riva, Hyman, Winter, & Guadagnini, 2014). The skewness of the velocity distribution (tested through H1) was not a key factor to determine discharge patterns, even though a simulation with more skewed velocity distribution was slightly closer to the experiment results. Other cases with a more skewed exponential distribution and a log-normal velocity distribution were also tested (data not shown) but did not help in reproducing all the events. Because a parameter set that would improve the simulation results could not be identified through manual calibration, the persistence in particle velocities was introduced (using TPM).

### 7.2 The velocity persistence improved tracer simulation (H2)

The use of the TPM (H2) allowed examining two extreme cases: velocity exchange at every time step, Ex\(_{H}\), and a relatively low exchange, Ex\(_{L}\). The low exchange scenario conceptually represents a small exchange between slow and fast pathways, with pore velocities that have high spatial autocorrelation, as presented in the work of Gerke and van Genuchten (1996). Assuming that the water particles tend to remain in their current velocity classes improved the capability of MIPs to simulate the tracer movement through the soil but only in combination with the assumption of immobile water and variable FC.

The improvement in the Cl\(^{-}\) output simulation using the TPMs (while immobile water was allowed) is attributed to a more realistic representation of the soil column microstructure. This concept is explained in Figure 6, where the column using 10 dotted lines...
representing the pores is represented in the two different extreme cases hereby analysed: with ExH, flowpaths are short and not interconnected, as each particle changes velocity at each time step (Figure 3a). In this case, the average length that a water particle would cover during a time step of 1 min would be ~6 mm. With ExL, the particles tend to keep their velocities; in this case, the average distance covered by fast particles per time step would be ~12 mm (red) and ~0.1 mm by slow particles (blue).

Connectivity often allows or denies the possibility of connectedness of larger more continuous pores, including any macropores (Beven & Germann, 1982). Our tests show that what is important in reproducing the experiment is not only the faster velocities in such pores but also the processes of water exchange and connectivity. In other words, because we will generally never be able to know the actual structure of a soil in situ, this is a way of improving understanding of the complex mixing processes involved (Jarvis, 2016; Lin, 2010). After all, many different types of preferential flows can be occurring at the same time, including finger flow, bypass flow, and macropore flow (Beven, 2018; Beven & Germann, 2013; Beven & Germann, 1982).

### TABLE 5

| Scenario combinations | $R^2_{Qc}$ Mobile | $R^2_{Qc}$ FC | $R^2_{Cl^−}$ Mobile | $R^2_{Cl^−}$ FC |
|-----------------------|-------------------|---------------|----------------------|-----------------|
| $Sk_H, Ex_H$          | .85               | .99           | .93                  | .93             |
| $Sk_L, Ex_H$          | .91               | .97           | .96                  | .90             |
| $Sk_H, Ex_L$          | .63               | .99           | .86                  | .95             |
| $Sk_L, Ex_L$          | .65               | .95           | .86                  | .90             |

Note. Each row represents the different combinations of scenarios with high and low velocity skewness ($Sk_H$ and $Sk_L$) and high and low exchange probability ($Ex_H$ and $Ex_L$), as shown in Figures 3 and 4.

### FIGURE 4

Simulation results for H1 and H2, as in Figure 3, including the immobile hypothesis, H3, through the FC parameter. Cumulative discharge normalized to the total input (a) and cumulative Cl\(^-\) export normalized to the total input Cl\(^-\) (b), plotted against the time steps when the measured discharge was greater than zero. Black solid lines show the measured data. Scenarios with high and low velocity skewness ($Sk_H$ and $Sk_L$) are shown with yellow and blue, respectively. Scenarios with high and low exchange probability ($Ex_H$ and $Ex_L$) are shown with open and filled circles, respectively. The infiltration events (Ev.1, etc.) are marked with grey dashed lines.

### TABLE 6

| Scenario combinations | $Q_c (h; p)$ Mobile | $Q_c (h; p)$ FC | $Cl^− (h; p)$ Mobile | $Cl^− (h; p)$ FC |
|-----------------------|---------------------|-----------------|----------------------|------------------|
| $Sk_H, Ex_H$          | 1; 01               | 0; .18          | 1; .04               | 1; .02           |
| $Sk_L, Ex_H$          | 1; 02               | 0; .13          | 0; .10               | 1; .00           |
| $Sk_H, Ex_L$          | 1; 00               | 0; .10          | 1; .02               | 0; .10           |
| $Sk_L, Ex_L$          | 1; 00               | 0; .10          | 1; .02               | 1; 00            |

Note. Each row represents the different combinations of scenarios with high and low velocity skewness ($Sk_H$ and $Sk_L$) and high and low exchange probability ($Ex_H$ and $Ex_L$), as shown in Figures 3–5.
Gerke, Germann, & Nieber, 2010; Krzeminska et al., 2013; Kung et al., 2000). Our strategy using different TPMs shows that MIPs has the potential to represent such complexity in an effective way. The TPMs, with low exchange between slow and fast pathways, suggesting that larger pore sizes have high spatial autocorrelation, effectively represent the connectedness of the faster flow pathways at this site.

**7.3 Immobile storage improved the model performance (H3)**

The immobile water hypothesis, H3, was explored by preventing water particles to move when water content drains to the value of $F_{CH3}$ (Section 5.1). This immobile water option is somewhat different to that normally assumed in dual porosity models but allowed for the...
retention of tracer and was important in improving the volume performance, with $R^2$ increasing for all simulations (Table 5).

Despite the good model performance for the outflow (celerity response) in all studied cases, the Cl$^-$ export was still not well represented in Events 3 and 4, with any of the tested models (i.e., the Cl$^-$ export was still overestimated). This suggests that some additional retention mechanism is prevailing: either to increase exchange with fully immobile storage or to include some geochemical retention process (though with salt tracer anion exclusion is more likely to reduce retention). Either will require additional parameters to be specified.

### 7.4 The soil microstructure changed during the experiments (H4)

None of the tested parameter combinations and distributions tested through H1, H2, and H3 were able to reproduce well both initial and final stages of the experiment. Based on a change in soil properties over time, as suggested in the work of Scaini et al. (2017), a time-variable FC concept was introduced through manual calibration of the FC$_{TM}$ (H4). The tests with FC$_{TM}$ allowed to better reproduce the experiment, improving both the modelled outflow, that is, the celerity response, and the modelled Cl$^-$ export, that matched closely at the end of the experiment (Figure 5). The change in FC was motivated by the unaccounted effects that the salt tracer addition might have on soil structure (Gharaibeh, Eltaif, & Shunnar, 2009; Holland, 1996). The presence of sodium in the percolating solution or in the ion-exchange complex has been frequently observed (qualitatively) to decrease permeability (Rengasamy & Olsson, 1991). Some studies on loamy-sand soil showed that a fivefold rise in electrical conductivity generates an increase in the exchangeable cations, responsible for an increase in dissolved organic carbon sorption processes (Setia, Rengasamy, & Marschner, 2013). Early studies demonstrated that (a) the salinity of percolating water causes dispersion or swelling of clay particles in the soil, which is the main mechanism responsible for a decrease in hydraulic conductivity (Pupisky & Shainberg, 1979) and (b) such “salt-dependency” of hydraulic conductivity could be modelled on salt water intrusion events (Mehnert & Jennings, 1985). Other studies supported such structural changes exploring the effects of salt-dependency on different textures and aggregates sizes (Benzon, Yolcu, Uysal, Lado, & Paz, 2009) and demonstrated the process of clogging of macropores under saline conditions (Basile, Buttafuoco, Mele, & Tedeschi, 2012).

This change in microstructure is supported by the different % outflow and Cl$^-$ exported in the experiment as compared with the modelled values under all tested hypotheses (Figures 3b and 4b). Evidence for a change in microstructure was observed as a visible change in slope of the outflow during Event 1, likely causing clogging in some of the pores near the surface and modifying the microstructure of the upper layer due to swelling of the clays (in this soil, about 20–25%, Section 2). This change was observed measuring the impact of immobile water regions in the study of Knorr, Maloszewski, and Stumpp (2016). The greatest modification of the microstructure is expected in earlier events and expected to be less for further water applications. This could be the reason why during Event 4, the slope was reduced to presalt experiment level.

The particles transported by water, due to the application system used for the experiment, might have led to a simple obstruction of the pores after the first applications. Such an effect should be lower than rain-splash effects on bare natural soil surfaces, as rainfall has higher energy than the system used here.

### 8 CONCLUSIONS

Simulation of both hydrograph (celerity response) and tracer breakthrough (velocity response) is one important step required for solving the old water paradox. Tracer movement through the soil is the most useful way for estimating velocities. We often lack information on the influence of soil properties on tracer mobility, and tracer experiments used in combination to particle tracking models can explore this issue. For this purpose, a 1-D version of the MIPs model was used to reproduce both flow and transport during a column tracer experiment.

The laboratory column experiment suggested that applying NaCl as tracer solution modified the pore structure and, consequently, the apparent FC, during the experiment. Four hypotheses were explored with MIPs by (a) testing the effect of a variation in the shape of velocity distribution, (b) testing the TPMs influence on model performance, (c) testing the presence of immobile storage, and (d) testing a time-variable FC.

MIPs provided a good representation of the volume outflow during the experiment. The hypotheses testing showed that

1. the use of a more skewed velocity distribution improved slightly the ability to reproduce the evolution of the pore structure;
2. the use of TPMs improved the capacity of the model to predict the tracer breakthrough and showed that the macropore structures connectedness controls the infiltration of water through the soil, rather than the changes within the velocity in the macropore space;
3. the best model performance was obtained with the inclusion of a local immobile storage;
4. the time-variable FC parameter allowed the experimental data to be completely reproduced.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author, A. S., upon reasonable request.

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