Velocity and celerity in a forested headwater catchment: a combined experimental and modelling approach

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Velocity and celerity in a forested headwater catchment: a combined experimental and modelling approach

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Abstract

One of the most important issues in modern hydrology is to improve our understanding of the release of old water during rainfall events. This thesis approaches the problem of estimating velocities, a measure of water transport, and celerities, a measure of the hydrograph response. We aim at measuring and interpreting estimates of velocity and celerity in a consistent way using in situ data. For this purpose, we performed multi-tracer irrigation experiments at different scales, from soil column to hillslope, to a sub-catchment scale analysis in a forested headwater catchment characterised by fractured bedrock. Our field experiments proved the importance of bedrock cleavage orientation in controlling subsurface flow direction and demonstrated the importance of quantifying the extent of fractures as well as their orientation relative to dominant topographically related flowpaths. An undisturbed soil column experiment was used in a hypothesis-testing framework in combination with a Multiple Interacting Pathways (MIPs) model. The use of a transition probability matrix (TPM) in combination with immobile water and variable field capacity parameters allowed the representation both volume and tracer dynamics. A framework to estimate both velocities and celerities using commonly-available hydrometric and tracer data is presented, emphasising the importance of choosing appropriate distance information as it can strongly influence the estimates and thereby the interpretation of controls on catchment function. The analysis of velocities and celerities at different spatial and temporal scales showed that the relationship between velocity and celerity shows a positive relation at the stream outlet. The experimentally-derived velocities and celerities metrics hereby explored have the potential to contribute to the evaluation hypothesis regarding catchment storage and release of water, by providing a direct comparison of what controls the old-water paradox.

Declaration

I declare that this thesis is my own work and has not been submitted in any form for the award of a higher degree elsewhere.
A la me fameute
Ca no mi lasè mai di besole
Nencje cuànt chi mi piart par da bon

Lorenzo Mattotti, Hansel & Gretel, 2007, the New Yorker. Detail of rippling water.
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When I was a kid I was fascinated by water. I used to spend hours playing around the artesian well at home, testing the capacity of my blood to keep my hands and feet at a decent temperature. I used to make my grandma upset.

I deeply admired her capacity of keeping her arms in the cold water for an amount of time that would bring anybody else to tears.

The movement of water captured my interest again for the work presented here. Instead of artesian water moving through my fingers, water moving through the soil is the main aim of this work. And rather than feeling the water through my skin, I have used more abstract metrics to gauge the water’s movement.

Much of our work in hydrology is focused on the movement of rainfall through a watershed – and we have explained the apparently contradictory quick rise of streams after rainfall and the long time (months, years even!) that water resides in catchments using the concepts of velocity and celerity. The difference between velocity and celerity and their relationship is one of the ultimate challenges of modern hydrology. Velocity and celerity are both linked to the concept of “speed”, but the terms are quite specific. In hydrology, we borrow the “hydraulic” definition of celerity, which goes somewhat like this: it is a measure of the impact of a perturbation on a channel. When it rains, in the soil we have a similar effect: water residing in the soil gets “pushed” by the “new” water coming in rain form. The result of this is that we can quantify the “push” with which water infiltrates in the soil during a rainfall event. This is called celerity, and it depends on how much water resides in the soil in the first place, and how much space there is yet to be filled.
during such “pushing”. Now, the measure of the movement of this new water entering the soil is different. Such new water will have a range of velocities depending not only on the amount of water that already occupies the space, but also how big the pores are, and how easy it is for water to move through them.

Ultimately, we can say that celerity is responsible for increases and decreases in stream discharge (the hydrograph), while velocity controls how old is the water reaching the stream at a given time.

So why do we need to keep these measures separate? Predicting the hydrograph response (celerity), given a certain amount of rainfall, can be done quite easily with modern modelling frameworks. However, equifinality is always around the corner: models can be parameterised in many ways to make a good approximation of the hydrograph, so which parameterisation is actually happening? I think of equifinality as a number of possibilities. From A I can reach B by taking different paths. Now, each path is different as some may be longer than others, some nicer than others, etc., but the point is that there is more than one way to get from one point to the other, they are all possible. In the same way, the water that contributes to the rise of a stream can come from different parts of the area conveyed to that stream.

When we are interested in measuring water in the soil, we have an additional issue to solve: water “disappears” to our eyes when it infiltrates in the soil. The invisibility of water inside the soil makes measuring things more difficult, but also more interesting.

To measure how much water comes from which part of the catchment, we need to design good experiments that allow us to measure velocities as well as possible, to try to understand which is the path that is taken by water. In order to do this, we can artificially apply water, but we need to know how to track the water we are adding. This is usually done by means of substances that can be dissolved in water, in particular salt tracers.

We performed experiments in this way, and as often happens, we found out that all our efforts brought little (that was 2014, my heart-breaking Experiment 1).
Experiment 2, in 2015, one year of experiences later, produced a dataset to work with.

I think you now have the means to understand most of the scientific content of my 4-year journey. No matter what path you take and which speed you go, I hope you enjoy every bit of it.
1 INTRODUCTION

Hydrology is a naturally multidisciplinary science – with direct, complex interactions with other sciences that can be merged within the water science domain. Geology, geophysics, climate sciences, chemistry, biology, ecology are deeply connected to the water cycle (McCurley and Jawitz, 2017). Such a complex network of disciplines makes hydrology a fascinating science.

Socially important hydrology issues are often linked to drought and flooding, the distribution of which in space and time is becoming more dramatic due to climate change. The urbanised water world, characterised by channelized and/or constrained water bodies, is leading to an increase of hazards due to land use, land cover and climate change (Alfieri et al., 2016). Human activities lead to (i) changes in temperature and water regimes, (ii) water quality issues and (iii) simplified natural systems with reduced gradients and corridors which can have a dramatic effect on natural systems and their ecology (e.g. eutrophication, pollution, change in habitat, reduced species diversity through the world), generating hazards related to pollution or flooding (including flash floods) (Schwarzenbach et al., 2006; Lin, 2010a).

Understanding water systems is a necessary first step to predict and improve the relationship between human activities and the environment. One of the most important scales of study is represented by headwater catchments, where most runoff is generated and where rivers take form.

Small forested catchments have been studied to address some of the most simple but difficult (and more frequently asked) questions of all: Where does water come from? How is water getting to the stream? What are the mechanisms that control such processes? Despite the simplicity behind these questions, much remains to be discovered to correctly understand and predict runoff generation processes.

1.1 RUNOFF HYDROLOGY: WHERE DO WE STAND?

The mechanisms underlying water transfer from rainfall to runoff are the essential components of the hydrological sciences. The hydrograph is the measure of the magnitude of streamflow change due to precipitation, and its occurrence and
shape are controlled by runoff generation processes, often chained one to another to define the processes that control how water reaches the stream. The most significant stream runoff generation processes, indicated in Figure 1, are:

(i) Long-term sources, mostly related to drainage processes, usually combined in the term baseflow,

(ii) surface runoff (overland flow), that can be due to saturation excess or infiltration excess, including the particular case of return flow – typical of riparian areas and valley bottoms (Horton, 1933; Genereux et al., 1993; Reeves et al., 1996; Lin et al., 2006),

(iii) direct precipitation falling on and in the vicinities of the stream and

(iv) subsurface stormflow (Anderson et al., 1997; Dunne and Black, 1970; Easton et al., 2008; Mosley, 1982; Whipkey, 1965).

Subsurface stormflow usually dominates the hydrograph response in deep soils characterised by high infiltration capacity (Sayama et al., 2011) but might represent a consistent contribution to runoff generation also in domains mainly controlled by other processes (McDonnell et al., 2007). Flow in the soil matrix can be slow but over time may generate the dominant flux (Tyner et al., 2007).

Figure 1. Sketch of runoff generation processes components based on (i) baseflow, (ii) overland flow, including the particular case of the return flow, (iii) direct precipitation on channel, (iv) subsurface stormflow, where water infiltrates and forms lateral flow contribution to channel stormflow, including the occurrence of preferential flow through macropores. The process of evapotranspiration (ET) is also shown as fundamental part of the water balance.
Additional mechanisms can occur across runoff generation processes and rapidly induce saturation at depth and mixing between subsurface hydrologic components (Gilman and Newson, 1980; Jones and Crane, 1984; Uchida et al., 2005; Beven, 2010). Such processes take place both in the soil matrix and in soil cracks, earthworm burrows, root channels, and include macropore flow and bypass flow (Beven and Germann, 1982). These processes are generally referred to as preferential flow, defined by the movement of water and solutes while bypassing a fraction of the matrix, leading to a non-uniform wetting front.

Evapotranspiration is a large part of the water balance in forested catchments, and the transpiration component dominates in many drier catchments (Teuling et al., 2006a, 2006b; Moore et al., 2011). Losses by evapotranspiration affect storage and baseflow dynamics.

1.1.1 A heterogeneous system

In catchments with predominantly subsurface flow, our ability to quantify, model or infer water flow paths is greatly impaired by subsurface heterogeneities. The spatial and temporal heterogeneity of soil and bedrock structures are known to control the subsurface hydrologic response that often dominates runoff generation (Graham et al., 2010; McDonnell et al., 2007; Zehe and Sivapalan, 2009). But what are these heterogeneities and what do they imply?

A linear response occurs when any increment of effective rainfall produces a response characterised by an increment of discharge of the same magnitude, i.e. the rainfall-discharge relationship is linear (Beven, 2012a). In most cases, this is not the case: particularly in the unsaturated zone, typically the soil overlying a water table or impermeable layer, the behaviour of small-scale hydrological processes is highly non-linear both temporally, during wetting and drying phases, and spatially, with dynamic contributing areas leading to non-linearity in hydrograph response (McGuire and McDonnell, 2010; Beven, 2012a). Such non-linearities control storage-discharge hysteresis (the change of their relationship in wetting and drying conditions) and are linked to antecedent moisture conditions (Beven, 2006; Davies and Beven, 2015;
Norbiato and Borga, 2008; Zuecco et al., 2015), and the change of flow velocities and celerities with discharge (Beven, 2012a). Hysteresis occurs if input-output relationships depend on the timing and history of the input and not just the value or magnitude of the input alone (Norbiato and Borga, 2008).

In addition to non-linear responses, the storage-discharge response can also change over time (i.e. is non-stationary) (Beven, 2012a; Klaus et al., 2015).

The assumption of equilibrium of the soil processes is in theory applicable at the scale of which detailed information on properties and structure is available (Ross and Smettem, 2000). The equilibrium then depends on the scale at which the Darcy law might hold, so that some local pressures and gradients can be defined, as there can be heterogeneity and preferential flows even in well sorted soils. The equilibrium could hold at local scale but not when averaged over larger (plot to field) scales because of non-linearity, also due to the non-linear shape of the hydraulic conductivity function, which shows dramatic increases with increasing water content (Šimůnek et al., 2003). The non-equilibrium flow in structured soils is defined as a flow where ‘infiltrating water does not have sufficient time to equilibrate with slowly moving resident water in the bulk of the soil matrix’ (Jarvis, 1998) and is related to preferential flows (Section 1.1.1).

Determining soil or runoff generation parameters in real case studies is complicated due to field evidence of heterogeneity of soil properties, preferential flow domains, and hysteresis (Beven and Germann, 1982). Therefore, exploring the interplay between non-linear, non-stationary, heterogeneous and hysteresis-driven processes represents a key research frontier in understanding how catchments process water and solutes (Birkel and Soulsby, 2015).

1.1.2 Scaling up processes

At any scale of study, there is the need for provide some assumptions related to the boundary conditions, defined by the fluxes occurring at the boundaries of each discrete element analysed. Boundary conditions can be time-variant and are extremely difficult to predict, but highly important in order to characterise and predict runoff dynamics at any given scale (Beven, 2006). The importance of lower
boundary has recently developed into studies trying to employ statistical methods to predict bedrock depth (Gomes et al., 2016).

Nested catchments studies are used to investigate how the dominant runoff generation processes change with scale. Such studies attempt at identifying how differences across scales and other characteristics may influence runoff (Didszun and Uhlenbrook, 2008; Jencso et al., 2010; Ockenden and Chappell, 2011).

Given the complexity of runoff dynamics, small-scale studies are often used to gather data that represent and describe runoff processes at larger scales. Laboratory-scale analyses allow the precise measurement of intermediate states as well as the (partial) control of boundary conditions. Undisturbed soil columns are often considered small-scale field experiments conducted under such simplified conditions. Intermediate scale experiments at the plot scale can be useful in that boundary conditions can be controlled partially though heterogeneities are still a critical issue.

In the field, the hillslope scale is often used to perform experiments as well as build and test models of the hydrological response. The term hillslope is general, and indicates a “slice” of catchment that goes from the watershed divide to the stream bed. A typical hillslope is characterised by a layered structure including vegetation, soil, saprolite (partially weathered parent material), weathered bedrock, and fresh bedrock (Lin, 2010a; Lorz et al., 2011). At the hillslope scale, complex interactions between matrix and preferential flow processes in the soil lead to rapid runoff, and controls on biogeochemical export etc. (Woods and Rowe, 1996; McGlynn et al., 2002). Beyond the invoked mechanisms that rapidly transmit water to the bedrock (preferential flow etc.), part of the complexity in hillslope runoff response is due to bedrock topography and bedrock fracture characteristics (McDonnell et al., 1996; Freer et al., 2002). Having a good knowledge on the soil structure at hillslope and catchment scale is critical, but understanding bedrock characteristics often requires very specific knowledge and high resolution data (Singhal and Gupta, 2010; Shangguan et al., 2017).
1.1.3 Tracer hydrology and the old-water paradox

Geochemical properties and tracers characteristics allow us to characterise water (and solutes) moving through the soil (Reeves and Beven, 1990; Kendall and McDonnell, 1998). Tracer limitations lie in the impossibility of detecting tracer concentrations below a certain threshold (depending on the sampling technique), and feasibility and time resolution of the sampled water (Flury and Wai, 2003; Gooseff and McGlynn, 2005; Gerke et al., 2013).

Since the advent of tracers in hydrology, we have been able to characterise the age of water and its sources, in terms of unique water signatures that could be mapped back to geographic locations by means of their chemical concentrations.

As it became clear that pre-event water could dominate storm runoff (Sklash et al., 1976) and that contributions of pre-event water could generate a response by displacement into faster flow paths (Pearce et al., 1986), stormflow generation studies focused on addressing solute transport characteristics and sources during and between storm events (Hornberger et al., 1991; Wilson et al., 1991). Such information greatly facilitated the characterisation of mixing, in particular the application of end-member mixing analysis, EMMA (Hooper et al., 1990).

Hydrologic tracers also led to the development of methods to separate the hydrograph into the temporal changes in composition from different sources (Buttle,
1994; Klaus and McDonnell, 2013) as well as concentration/discharge hysteresis (Evans and Davies, 1998), often trying to support existing hydrologic process theory rather than evaluating or testing how such theories apply to different case studies (Bishop et al., 2004).

Tracer analysis paved the way for the old-water paradox (McDonnell, 1990): water that has been residing in the catchment is released quickly during events, and even from varying sources with complex geochemical signatures (Kirchner, 2003). One of the most important issues in hydrology in the last decades has focused on factors controlling such movement through subsurface flow paths.

In discussing the double water paradox, Kirchner (2003) expressed the dualism between water and geochemical response in two questions: “How do catchments store water for weeks or months, but then release it in minutes or hours in response to rainfall inputs?” and “How do catchments store ‘old’ water for long periods, but then release it rapidly during storm events, and vary its chemistry according to the flow regime?”

1.1.4 Velocity and celerity frameworks

Resolving the double paradox is of importance for hydrology’s role in supporting other catchment science disciplines and the resolution of specific environmental questions (Bishop et al., 2004). We currently evaluate catchment responses based on hydrograph response, time source (old and new water components) and flow path, using different methods for each (Barthold and Woods, 2015). However, storm runoff occurs on a different time scale to that of the water flowing slowly through the catchment (i.e. the long-term drainage and ET component, Section 1.1.1), yet we typically model only the rainfall/runoff components, effectively only half of the catchment transport story.

McDonnell and Beven (2014) recently stressed the importance of characterising both tracer velocities, the measure of how fast pore water moves, and celerities, the measure of how fast the storage of water responds to a perturbation, in response to a rainfall event. This is critical as it helps explain the old-water paradox where streams can respond quickly to rainfall inputs but with water that has resided in the
catchment for weeks, months or years (Beven, 1989a; Kirchner, 2003). Beyond increased process understanding, the characterisation of velocities and celerities is necessary to implement physically-reasonable model interpretations of flow at the hillslope and catchment scales.

### 1.1.5 Transit times

The transit or travel time is the time spent by water travelling through a catchment until reaching the stream network, i.e. the elapsed time between entry and exit as discharge at the outlet. The residence time is the elapsed time from the time of water entry into the catchment for water stored in the catchment. Transit time distributions (TTD) reflect how precipitation from different storms is stored and mixed as it is transported to the stream, i.e. how catchments retain and release water and solutes, reflecting the advection (delay) and dispersion (spreading) of tracers due to transport processes (Nyberg et al., 1999; McGuire and McDonnell, 2006; McGuire et al., 2007). Both concepts – residence times and TTDs – describe the age structure and the chemical composition of rainfall, discharge, storage, soil water (Hrachowitz et al., 2016), accounting for how different “ages” of water are mixed in the soil: a conservative tracer input travelling through the catchment until reaching the outlet will result into a damped and lagged signal with less high frequency variation (McGuire and McDonnell, 2006; Tetzlaff et al., 2015).

In transit time theory, the distribution of input chemistry (usually isotopes) and output chemistry are related by means of a transfer function, that can be defined to quantify how catchments store and release water and solutes based on transit times (Rinaldo et al., 2015). Catchment travel time distributions can therefore be described by the mean travel time and the shape of the distribution around the mean (Klaus et al., 2015).

Directly tracking the age of water (TTD) as well as the magnitude and shape of the hydrograph response solves for mass and transport at the same time, reflecting the difference between velocities and celerities (i.e. the relationship between recharge and flow). In order to adequately model such a response, assumptions must be made about the velocity distribution associated with the mean velocity and the
continuity equation. In order to improve in this direction, the non-stationary characteristics of transit time distributions needs to be taken into account (Davies and Beven, 2012), as attempted in recent developments (Soulsby et al., 2015; Kirchner, 2016a; Pangle et al., 2017). Transit times have the potential of assisting water quality management as well as build on understanding and characterisation at the larger scale (Hrachowitz et al., 2016) and Kirchner, (2016b), respectively).

1.1.6 Hypothesis testing in hydrology

In hydrology, there are a few methods currently used to rank the performances of experimental and modelling results. Statistical methods based on interval confidence and thresholds – are the most employed strategy.

Modelling can be seen as a sort of “uncertain mapping of the catchment in the modelling space” (Beven, 2001). In order to account for uncertainties, and the inherent difficulties of the required measurements, one can identify parameter sets using the model as a hypothesis testing framework, to infer which types of model parameterisation are consistent with the available data (Beven, 2001, 2012b). In this framework, different model parameterisations represent multiple working hypotheses that need to be tested against observed data (Chamberlin, 1890; Elliott and Brook, 2007). Such process of detection considers uncertainty explicitly (as discussed in Beven, 2008) but does not overcome the possibility of multiple parameter sets giving acceptable results – the equifinality issue (Beven, 2006a, 2006b).

1.2 KNOWLEDGE GAP AND CHALLENGES

In the previous section, we had an overview of the most important phases in hydrological discovery to date. Hydrology is challenging because small-scale complexity translates into relative simplicity at the larger scale: the hydrograph (Beven, 1987). Ultimately, there are a few areas that we need to improve in the science. This work tries to address some of the issues of our discipline, described below.
1.2.1 Can we measure it all?

To address the heterogeneity of surface and subsurface flow paths and flow-velocity distributions, we require measurement of all the surface and subsurface properties involved. Improved experimental techniques are available thanks to the use of field portable equipments allowing in situ analysis and high resolution measurements (for a review, see Gałuszka et al., 2015). Even the use of the most modern techniques, though, are limited to a certain domain, and investigating processes below the soil surface remains challenging. Moreover, invariant measures and high complexity makes it difficult to transfer knowledge across scales. Even if we could really measure it all, we would require more information to scale measurements across systems.

A key issue is to scale up processes that can only be measured locally, as most techniques are applicable only at small scales. Small scale studies are really necessary to help understand responses at catchment scales of interest for useful applications.

1.2.2 Boundary conditions - one obstacle to overcome

Boundary conditions represent the fluxes for the system under observation. It is indeed crucial to understand the limits of a given hydrological compartment under study, both in experimental and modelling hydrology. As most of our systems are located below the soil surface, one of the most challenging parts of all is to hypothesise/measure such boundaries. The more structured the system, the more complex it is to define its boundary conditions (laboratory experiments have usually constraints of their own but represent a simplification of real-case studies).

In particular, recent studies have recognized the importance of identifying runoff generating mechanisms governed by fractured bedrock hydrogeology (Banks et al., 2009; Hale et al., 2016). Bedrock, previously often assumed to be impermeable, proved to be structurally responsible for important water exchanges in the subsurface (Tromp-van Meerveld et al., 2007; Gabrielli et al., 2012). In both experimental and modelling hydrology, we often lack understanding of how to deal with the lower boundary responsible in most cases for driving subsurface flow in the downslope direction.
1.2.3 Problems of estimation and representation of travel times, and the paradox

Many unknowns must be resolved to improve our understanding of how heterogeneity affects water travel time characteristics and hydrograph responses (Botter et al., 2010; Rinaldo et al., 2011). Estimating and representing travel times is complicated by the lack of information on the shape of the transit time distribution – also in relation to the limitations of the tracers used (Section 1.1.4). The relationship between old and new water in time is a requirement for solving the old-water paradox. An improved understanding on (i) transit time distribution and (ii) velocity/celerity differences is required.

Given the complex heterogeneities and preferential flow pathways observed in real systems, there is still a need for new concepts in hydrological modelling that allow for these complexities more directly, with the aim of reproducing and understanding real (complex) cases (Davies and Beven, 2012).

1.2.4 The issues of testing models as hypotheses

There is still some degree of confusion in determining how to define and use consistently a hypothesis testing framework, which hypotheses are worth testing, and how to best evaluate each hypothesis. Defining a consistent framework to evaluate which types of model parameterisation are consistent with the available data is challenging, and complicated by the nature of the processes involved, as they are non-linear and non-stationary.

One of the challenges is that if different hypothesis are built on modelling strategies, they might be referring to interdependent assumptions (and parameters), making it difficult to correctly evaluate each hypothesis in relation to the others (Neuweiler and Helmig, 2017). Statistical methods can come handy in evaluating different hypothesis. In particular, testing models by comparing performance indices and relating back to some degree to tested hypothesis has been a strategy employed in many studies (Fenicia et al., 2016).

One important issue related to the testing of models as different hypothesis relies on how to deal with the issue of equifinality, which is the occurrence of different sets of parameters sharing an equivalent evaluation of the acceptability
term (Beven, 2006). To avoid issues linked to real-system inner complexities, hypothesis testing frameworks should be evaluated using limits of acceptability as a tool to evaluate models (Beven, 2010, 2012b).

We can therefore say that hypothesis testing can be used to address uncertainty, but at same time requires dealing with the uncertainty associated with the hypothesis testing itself.

1.3 AIM AND RESEARCH QUESTIONS

This section presents the strategy followed in this work in order to address the key knowledge gaps presented in the previous section.

This research aims to generate insights into flow paths and mixing through a combined experimental and modelling approach that increases our understanding of flow and transport processes, i.e. the displacement of hydraulically connected water (celerity) as well as the water velocity and flow path. We follow a two-fold strategy combining sprinkling experiments with a model as a learning tool.

The main questions we address are:

a) What is the value of different measurement techniques to describe subsurface response to rainfall? i.e. How can we measure effectively velocities and celerities at similar scales? (referring to the knowledge gap defined in Section 1.2.1)

b) How do bedrock structural properties influence tracer transport from plot to stream? (referring to the boundary condition gap, Section 1.2.2)

c) What flow path does water take before reaching the hillslope outlet? (referring to the knowledge gap regarding travel times estimation, Section 1.2.3)

d) How can we represent these processes within a modelling framework? (referring to the knowledge gaps raised in Sections 1.2.3 and 1.2.4)

e) How do celerities and velocities relate to each other? (referring to Section 1.2.3).
Our strategy essentially consists of:

- Explore measurement techniques and modelling strategies that could be useful in addressing the velocity/CELERITY issue;
- Estimate the residence times of water at the plot-scale;
- Quantify the relative importance of subsurface stormflow at the hillslope scale;
- Generate hypotheses about the behaviour of the system and test them with a Multiple Interacting Pathways (MIPs) model (Davies et al., 2011);
- Explore the relationship between storage and discharge dynamics with a view to velocity and celerity estimation from point-based information.

1.4 MOTIVATION AND METHOD OUTLINE

This section presents the methodology used to perform the present research. For each of the knowledge gaps identified, we try and find means to address the research questions presented in Section 1.3. Our research is motivated by the following points:

a) Measurement issues: Often there is a mismatch between local measurements and distributed measurements, due to the methodological differences and uncertainties. Moreover, interpreting any kind of measure at any scale is complicated by its nature and associated uncertainty. Plot and hillslope scale are a good starting point as boundary conditions are in part controlled, and allow measuring the lumped effect of the processes involved (i.e. hillslope discharge or chemistry), but require assumptions on whether the study scale is representative for the scale of interest (catchment scale).

b) Boundary conditions: We saw that recent works showed that boundary conditions and in particular bedrock permeability structures might influence subsurface dynamics. Here we build on this and try to define a simple way to evaluate the possibility of a structure dominating the subsurface pathway other than topography. A lot of unknowns remain regarding the mechanisms controlling water release to the stream in fractured bedrock systems, and this
work attempts to estimate velocities and celerities and characterise their behaviour given their importance in understanding subsurface processes.

(c) Measuring celerities and velocities: The relationship between velocities and wave or wetting-front celerities is essential to understand how the catchment responds to rainfall and why old water can be mobilised quickly during rainfall events. Although the characterisation of velocities and celerities is important to infer processes governing streamflow generation (flow pathways and residence times), the relationship between velocity and celerity, estimated by means of experimental techniques, has not been widely explored. The main challenge we are facing is to show how to integrate in a simple way measures of celerity and velocity into hydrological studies. Given the importance of the relationship between velocities and celerities and the difficulty in representing both at the same time and at similar temporal and spatial scales, we explore the implications of representing velocities and celerities employing commonly used experimental techniques.

d) Testing the representation of celerity and velocity by means of an appropriate model structure that has to (i) track both water and tracer and (ii) be a useful tool for applying hypothesis testing to understand complex subsurface systems.

This work stems from these issues. It tests different measurement and estimate techniques to measure wetting front and tracer movement through the soil. Moreover, it tries to estimate in a scale-invariant way both the propagation of a wetting front and the movement of event water, in an effort of developing a more broad understanding of subsurface generation processes accounting for the old water paradox.

Addressing our research questions requires intensive field work which cannot be carried out on extensive areas. For this reason, we have focused our study on a single experimental location. Intensive investigations at individual locations have occasionally been criticized for not bringing generalizable insights (e.g. Gupta et al., 2014). Although some of the results of these investigations is catchment specific, we believe that there is much to be exported from such studies. In particular, much of
our current understanding of streamflow generation processes relies on experiments at heavily instrumented catchments, such as Maimai or Panola. Similarly, we think that the conceptual process understanding originating from our study can be generalized to similar locations. In addition, our study will help to better understand what is the value of various modern experimental techniques to infer dominant processes, which has general value.

1.5 STUDY SITE

This research is undertaken at the Weierbach experimental catchment in Luxembourg. The Weierbach catchment is located within the Attert catchment (Pfister et al., 2000). The main peculiarities of the Weierbach are (i) very high runoff coefficients, (ii) it is underlined by fractured slate bedrock, (iii) the occurrence of characteristics double peak hydrographs – a second, longer hydrograph rise mainly composed by old water (Juilleret et al., 2011; Martínez-Carreras et al., 2016; Pfister et al., 2017). In particular, the occurrence of double peaks is a sort of « mystery » that makes this site an intriguing platform to explore the old-water paradox. Indeed, despite having been studied for the last 20 years, there are still many unexplored questions regarding what controls the aforementioned peculiarities: (i) the characteristics of the lower boundary, including the role of the fractured bedrock; (ii) the processes involved in the double peak in the Weierbach catchment, and (iii) the main runoff generation mechanisms involved.

Figure 3. Photographs of the Weierbach catchment. (a) Beech (Fagus sylvatica) hillslope; (b) Douglas fir (Pseudotsuga mentziesii) and Norway spruce (Picea abies) hillslope; (c) Exposed fractured bedrock; (d) Weierbach stream and riparian area near the outlet.
1.6  STRUCTURE / THESIS OUTLINE

Experiments are designed and applied to provide data that allow to estimate velocities and celerities that are tested within an appropriate modeling strategy that accounts for both measures of flow and transport.

Each chapter tries to meet one or more of the aims of the overall project:

**Chapter 2** defines velocity and celerity and describes the representation of both in the modelling and experimental domain to date, presenting more in detail the issues of measuring and modelling velocities and celerities, describing what needs to be improved and introducing the modelling strategy chosen for the present study.

**Chapter 3** characterises the vertical directions of flow in terms of flow celerities and tracer velocities, meeting the first objective (to explore velocity and celerity measurement techniques and modelling strategies).

**Chapter 4** follows the journey of water infiltrating through the plot until reaching the stream, analysing tracer transport from plot to stream and how it is influenced by bedrock cleavage orientation, meeting the objective of estimating the residence times of water at the plot-scale and the bedrock boundary issue.

**Chapter 5** describes how the generated data are used within a model to quantify leaching capacity of the soil and the velocity properties of the shallow soil, meeting the objective of generating hypotheses about the behaviour of the system and test them at column scale.

**Chapter 6** discusses storage/discharge relationships and explores the shape of the relationship between velocity and celerity. Such study meets the objective of exploring how measurement dynamics can be employed to understand catchment scale release of water during natural rainfall events.
2 VELOCITY AND CELERITY

The main concept described in this work is based on the difference between celerity and velocity. In the following sections, we will define both terms and discuss the implications of representing celerity and velocity in modelling frameworks, and the issues of measuring them both in the field.

2.1 A SIMPLE DEFINITION OF VELOCITY AND CELERITY

In Chapter 1, we introduced the main challenges in hydrology, showing in particular the complexity of (i) estimating and representing transit times, and (ii) solving the old-water paradox. One way to overcome the effects of heterogeneities in the unsaturated zone at the hillslope and catchment scales is to incorporate tracer observations that provide information about velocity distributions, expressing the effect of subsurface heterogeneities (Rinaldo et al., 2011) and simultaneous derivation of celerities from water content, piezometer and discharge responses (McDonnell and Beven 2014).

Advective flow processes, like preferential subsurface flow, are characterized by the movement of individual water particles due to the hydraulic gradient (Berne et al., 2005). Usually, the majority of subsurface flow contributing to stream flow is generated by diffuse flow processes, like groundwater responses (Berne et al., 2005), driven by the pressure head and the resulting translation of a pressure wave (Lighthill and Whitham, 1955; Henderson and Wooding, 1964; Beven, 1989a; Hrachowitz et al., 2013). Therefore, water velocities and the pore spaces through which they travel control the travel time and residence time distributions (Rinaldo et al., 2011; Kirchner, 2016b). Conversely, the hydrograph response is controlled by celerities of the pressure responses and the effective storage that is filled and emptied as the wetting front progresses into the soil and the water tables rises and falls (Beven, 2010; McDonnell and Beven, 2014).
Figure 4. One-dimensional sketch of a schematic soil box showing the difference between celerity and velocity estimated in this paper. The response to the sprinkling event using traced water (a) is shown. A wetting front is generated as a consequence to the pressure given by the water input (b). A process of displacement moves the water stored in the soil (c1). Bypassing flow occurs when traced water moves through preferential flow reaching the measurement point in correspondence with, or even “before”, the wetting front (c2). Modified from (Scaini et al., 2017a).

Celerity as a concept is widely used in the hydraulic community (see for a definition Gonwa and Kavvas, 1986). In this framework, only at critical flow (Froude number equal to 1) the velocity coincides with the celerity, while the supercritical (Froude number higher than 1) and subcritical flow (Froude number lower than 1) are characterised by velocity higher than celerity and vice-versa, respectively. Other formulations were summarised for the relationships between mean velocity and celerity under different types of flow by McDonnell and Beven (2014). A nice way of exploring the concept of a wave propagation (celerity) response can be to track down the wave signal propagated by natural hazards such as earthquakes (Manga, 2003; Montgomery and Manga, 2003; Mohr et al., 2012). Celerity formulations were
introduced into hydrological studies to deal with the non-linearity of unsaturated and saturated responses (Green and Ampt, 1911; Beven, 1981; Torres et al., 1998; Rasmussen et al., 2000).

Through the last decades, tracer studies showed the differences between the time scale of the celerity of the discharge response and the time scale of the pore velocity of water, and some recent model developments seem to have managed to go beyond the increase in parameters that including tracer information necessarily implies (recently reviewed by Birkel and Soulsby, 2015). Recent work has also introduced the need for experimentally-derived estimates of tracer velocities in the spatial and temporal evolution of stream flow (Benettin et al., 2015; Bergstrom et al., 2016).

Indeed, the changes in velocities and celerities with discharge are one of the causes of non-linearity, and velocity and celerity distributions are expected to differ from each other (Hrachowitz et al., 2016). Ultimately, achieving accurate estimates of tracer velocities and wetting front celerities would mean that process representations are more likely to be, in the words of Kirchner (2006), right for the right reasons (see also Beven, 2010; McDonnell and Beven, 2014).

2.2 REPRESENTING CELERITY AND VELOCITY WITHIN MODELS

In order to characterise celerity and velocity in a consistent way, adequate modelling strategies are required that can solve for both flux and transport. In this section, we will go through the modelling strategies adopted so far in hydrology and how we managed to characterise both velocities and celerities.

2.2.1 Modelling runoff response

In the field of hydrology, modelling has been an important resource to improve the understanding of runoff generation, and its time distribution. Many different types of models are available, often classified as lumped or distributed, deterministic or stochastic, plus new approaches that have been emerging from other disciplines like the fuzzy logic (Rajaram, 2016).
The continuum approach is the foundation of model hydrology, as it represents the response of the hydrograph to rainfall. The continuum approach is based on the Darcy-Richards equations (Freeze and Harlan, 1969), based on the linear relationship between flow velocity and hydraulic gradient, with a constant of proportionality called the hydraulic conductivity. In the unsaturated flow, the same relationship is assumed to be linear but is assumed to depend on a hydraulic conductivity that varies in a non-linear way with the moisture content (Richards, 1931). Such formulation was solved using many different approaches (Zehe and Jackisch, 2016).

As we know that most hydrologic responses are non-stationary (time-variant, Chapter 1), system representation requires a more complex framework to be characterised (Milly et al., 2008). This issue emerged as calibration proved to be effective in reproducing rainfall-runoff response but with poor representation of the processes involved - as measured in the field or hypothesised (Christophersen et al., 1993). In an effort to evolve in process understanding, an alternative blueprint taking into account equifinality issues was proposed by (Beven, 2002).

In order to move beyond the issues related to the classic formulation of the continuum approach, formulations accounting for preferential flow domains (Chapter 1) were introduced (revised in Šimůnek et al., 2003). In order to deal with transport, additional formulations are required, which are normally the advection-dispersion equations, ADE (LaBolle et al., 1998). Such formulations, accounting for the transport with the velocity of the flow pathways (advection) and the variation in transport as a result of a flow velocity variation (dispersion), provide Gaussian distributions of transport (in space).

Through the last 20 years, dual-porosity and dual-permeability formulations have been implemented. From the conceptual point of view, such formulations include two domains characterised by different hydraulic and transport properties, which interact with each other through an exchange term (Beven and Germann, 1981; Gerke and van Genuchten, 1993, 1996). In this way, both water and solute movement can be characterised by adding a formulation for transport dealing with parameters related, for instance, to mobile and immobile water. In a simplified way, the dual-porosity framework assumes stagnant flow in the matrix, while the dual-
permeability theory invokes active matrix flow movement. Both multi-porosity and multi-permeability models can be used to describe preferential flow through macropores and fractures (Šimůnek et al., 2003; Beven and Germann, 2013).

2.2.2 The Representative Elementary Watershed (REW) and particle tracking concepts

Particle tracking methods were introduced to calculate and visualise advective and dispersive transport within flow fields obtained from the numerical solution of the Richards equation (Maier and Bürger, 2013). In particle tracking models, a particle is a discrete volume with certain properties which are carried within its movement in the domain, allowing to track water properties through the modelling domain (Davies et al., 2011, 2013; Tschiesche, 2012; Maier and Bürger, 2013; Henri and Fernàndez-Garcia, 2014; Zehe and Jackisch, 2016). Using particle tracking to represent provide a solution for both water and associated tracer was first suggested under kinematic assumptions by Beven et al. (1989). An alternative framework was suggested in the subsystems and moving packets (SAMP) framework was proven able to determine new and old water components as well as solute in a single framework (Ewen, 1996; Ewen and O’Donnell, 1997).

Other frameworks analysing both celerity, the hydrograph, and velocity distributions, given by tracer concentrations, have recently proven to be effective in improving our understanding on celerity-velocity interactions (Davies et al., 2011, 2013; Laine-Kaulio et al., 2014; Beven and Davies, 2015; Scudeler et al., 2016). We rely on the Multiple Interacting Pathways (MIPs) model, which uses a random particle tracking method to evolve the water and

2.2.3 The Multiple Interacting Pathways model

A recent promising model of catchment flow processes that provides a fully integrated framework for velocities and celerities is the Multiple Interacting Pathways model (MIPs). The MIPs model solves for both the hydrograph and tracer response (Davies et al., 2011) using particle tracking model to evolve the water and
tracer location, trajectory, and age, making it a useful tool for hypothesis testing in complex subsurface systems.

The MIPs model was first developed by (Beven et al., 1989). For 2 decades, there were no studies that built on such a modelling strategy. The MIPs model was then applied to a roofed hillslope located in the Gardsjon catchment in Northern Sweden and was able to produce good simulations of both flow and tracers at both plot and small catchment scales (Davies et al., 2011, 2013).

The MIPs framework allows the positions and properties of water particles to be directly tracked and it simulates transport and flow simultaneously. In this way, the hydrograph is solved for mass and transport at the same time, while taking into account the non-stationarity of the travel time distributions. Particle characteristics, such as age information or concentration are carried along with each particle. Particle velocities are chosen with a random component according to assumptions about the local velocity distribution. Those assumptions are not limited to Gaussian deviations from the local mean velocity but can be chosen to reflect the possibility of slow matrix velocities and preferential flow pathways. The approach necessarily maintains continuity, as all input particles to the system are tracked until they leave. The assumptions can be extended to allow for interactions between pathways, such as the displacement of matrix particles into faster flow pathways.

A few other studies followed with (i) a comparison between the MIPs framework and a classic kinematic wave approach (Davies and Beven, 2012) and (ii) the first development of a 3D MIPs model, applied to the whole Gardsjon catchment (Davies et al., 2013). The ability of the MIPs model to describe the scale-dependent, hysteretic relationships between flux and storage has been recently demonstrated (Davies and Beven, 2015).

Simultaneously mapping flow and transport dynamics allows the non-linearity of catchment responses to be explored in terms of storage-response variable relationships (Beven and Davies, 2015; Davies and Beven, 2015). In this study, very promising results were obtained by the comparison between scaled versions of the catchment, and it was shown how scale affects flow responses and input, output and
storage residence time distributions, as well as the relationship between storage and water table levels hysteresis.

2.3 EXPLORING EXPERIMENT TECHNIQUES TO QUANTIFY CELERITY AND VELOCITY

How well we measure subsurface processes and pathways is ultimately determining how well we can model them, as hydrology as a field is measurement-limited (Beven, 1987; Burt and McDonnell, 2015). As knowledge regarding the necessary measurement data are limited, it is often a good practice to perform experiments through solute breakthrough experiments on undisturbed columns (Abdulkabir et al., 1996). In an undisturbed column, the structure of the soil is maintained, and the boundary conditions can be controlled respect to any scale in the field. The downside is that handling soil columns is technically complicated and can affect the experiments, due to artificial preferential flow paths, non-ideal injection technique, and unrealistic moisture regimes (Lewis and Sjöstrom, 2010). Indeed, extrapolating knowledge from any laboratory scale to any field scale is then an issue as the limited volume studied (assuming there are no artifacts linked to the handling of the soil cores) is only representative for that specific volume – and might be unrepresentative of the scale of study. Larger scales experiments, like plot scale, can be of use as they integrate over some of the heterogeneity at the column scale (even if there might be heterogeneity between plots).

In the field, sprinkling experiments carried out at trenched hillslopes are often used to characterise the vertical and lateral components of flow reaching different soil layers (McGlynn et al., 2002; Wienhöfer et al., 2009), while still allowing some control on rainfall characteristics and, only in part (respect to column scales), boundary conditions (McDonnell et al., 2007; Wienhöfer and Zehe, 2014).

2.3.1 Estimating celerity

For most studied catchments, there is usually some information regarding celerity, at least at the catchment scale: the hydrograph at the outlet.

In the field, celerity can be estimated using discharge measurements, for the hydrograph response, and groundwater wells, to measure water table response. In the unsaturated zone, soil moisture estimated using Time Domain Reflectometry
(TDR) (Topp et al., 1980) can be used to detect the arrival of a wetting front (Haga et al., 2005). As wetting fronts can be highly spatially variable, obtaining spatially highly resolved data with point measurements using TDR remains challenging and expensive (Vereecken et al., 2014). Other techniques that can be efficiently used to follow the wetting front through the soil are non-invasive and spatially distributed, like electromagnetic induction, fiber-optic approaches, Ground Penetrating Radar (GPR), and geophysical techniques (Loke and Barker, 1996; Kemna et al., 2002; Binley and Kemna, 2005; Selker et al., 2006; Binley et al., 2015). Each of these techniques present some limitations, and they are often used in complementary ways to improve their informative potential.

2.3.2 Estimating velocity through the use of tracers

Water residing in different zones and contributing to streamflow by different hydrologic pathways can be expected to have different chemical signatures. Therefore, stream chemistry is centred towards understanding which pathways are responsible for water movement until reaching the stream (Genereux et al., 1993). Information on velocity and the residence time of water require to be estimated in the field, and is often combined with the detection of tracers, either natural, or artificial. Following tracer movement in space and time corresponds to get information about its velocity properties. Even if such information are often used in hydrology to characterise water pathways (Graham and McDonnell, 2010; Perkins, 2011; Tyner et al., 2007), the estimation of velocity information from tracer measurements is anything but easy.

Some attempts of estimating subsurface pore water velocities have been effective at the plot and hillslope scale (Mosley, 1982; Sidle et al., 1995; Rodhe et al., 1996; Nyberg et al., 1999; McGuire and McDonnell, 2010). The determination of transport characteristics in groundwater has also been widely explored (Kalbus et al., 2006; Kahn et al., 2007; Phillips and Castro, 2013; Padilla et al., 2015), including studies performed on fractured bedrock systems (Cook et al., 1996; Onda et al., 2001; Padilla et al., 2014). For instance, the work of Kang et al. (2014) characterised the impact of velocity distribution and correlation on transport, using convergent and push-pull tracer tests at a fractured aquifer.
In order to obtain reasonable velocity estimates, the groundwater velocities should be computed between different wells using travel time and distance data (Freeze and Cherry, 1979) over a known flow direction line, which can be depending on subsurface stratification (Kalbus et al., 2006). The bedrock structures and characteristics can allow weathering reactions that will provide higher concentration of some of the chemical species involved (Neal et al., 1997). Tracers can be used to perform tests to determine flow velocity to the stream (Todd and Mays, 2005).

2.3.3 Types of tracers

Tracer studies are employed to understand how quickly, in what concentration and from what sources does water reach the stream. Tracers offer a tool to characterize water velocities and pathways even in complex, heterogeneous subsurface environments (McGuire and McDonnell, 2015). Tracer input-output relationships are used to estimate the transit-time distributions of water in the catchment (Nyberg et al., 1999; McGuire et al., 2007; Klaus et al., 2015) and can be useful to characterise flow paths (Trudgill et al., 1983; Wiencehöfer and Zehe, 2014). Tracers can be naturally present in the water molecule (H and O isotopes) (Sklash et al., 1976; Sklash, 1990), or artificial, actively introduced in the system (Kendall and McDonnell, 1998). Natural tracers include stable and radioactive isotopes of hydrogen, deuterium or “heavy water” and tritium (Martinec, 1975; Ogunkoya and Jenkins, 1991; Stewart et al., 2010; Stumpp et al., 2014), and radiogenic isotopes (Kendall and McDonnell, 1998; Moragues Quiroga et al., 2016). Isotopes of hydrogen can also be artificially injected (Kendall and McDonnell, 1998; Nyberg et al., 1999). The most common artificial tracers are dissolved in water and can be dyes and fluorescent tracers (Trudgill et al., 1983; Flury and Wai, 2003; Gerke et al., 2013), anions and cations as dissolved salts (Hornberger et al., 1991; Flury and Papritz, 1993), and fluorobenzoic acids (Bowman and Gibbens, 1992; Jaynes, 1994; Henderson et al., 1996; Reeves et al., 1996). A simple way of tracing water properties, in terms of concentration of solutes, is by measuring changes on electrical conductivity (Kobayashi, 1986), or alkalinity (Rodgers et al., 2004). Novel techniques allow an improved tracing strategy for properties that can be used as tracers, like temperature (Birkinshaw and Webb, 2010; Naranjo et al., 2013), and
drifting particles as lycopodium spores, diatoms, fluorescent particles, nanoparticles, and even DNA (Pfister et al., 2009; Foppen et al., 2011; Granger et al., 2011; Sharma et al., 2012; Hawkins et al., 2017).

2.3.4 Tracer interpretation

The interpretation of the tracer results is often complicated. Not only mixing with water residing in the soil, but also the direction and diffusion of tracer in the system generate uncertainty regarding what is being measured. The most problematic issue of tracer-based investigation is the soil water sampling. There are a few measuring techniques potentially useful, each of which have pros and cons. Geochemical processes, such as sorption/desorption, and root uptake affect measured concentrations (Weihermüller et al., 2007). Often, multiple tracer studies are performed to overcome issues related to the interpretation of the tracer results (Abdulkabir et al., 1996; Reeves et al., 1996; Mortensen et al., 2004; Abbott et al., 2016).

To measure changes in the soil due to the presence of natural and artificial tracer, many intrusive techniques were developed and used: suction lysimeters (Wagner, 1962) can be used to detect tracer arrival times (velocities) (Perkins et al., 2011), but the concentrations detected are expected to be a mix of mobile and relatively immobile water (Weihermüller et al., 2005). Some versions of the TDR probes can be used to infer electrical conductivity data as an indication of tracer arrival (Dalton et al., 1984; Persson, 1997).

2.3.5 The issues of choosing tracers

Different types of tracer should be employed according to the purpose. Employing any tracer should go with a deep knowledge regarding biochemical properties (i.e. solubility, interaction with other solutes, degradation due to different factors), detection limits and analysis costs and means, since each of them have pros and cons. For instance, the interpretation of most property-based tracers, like temperature or electrical conductivity, is complicated by water sources and flow path and geochemical interactions respectively. On the other hand, fluorescent tracers
tend to have very high sorptive properties and are sometimes photolytic (Gerke et al., 2013).

Depending on their nature, tracers can be near “ideal” in case of very low (or absent) natural abundance and conservative characteristics (Flury and Papritz, 1993; Nickus, 2001). Natural tracers, as they are part of the water molecule, are the “real” ideal tracers, but their interpretation is mined by spatial variability of rainfall input, interception effect on input concentration, and sources variability in concentration. Moreover, isotopic water analysers are costly and require expert use. Amongst the artificial tracers, bromide is the closer to ideal thanks to its high solubility, low sorption and usually low natural abundance (Flury and Papritz, 1993).

2.4 INTEGRATING Celerity AND VELOCITY ESTIMATED WITH A DATA-BASED APPROACH

The following chapters apply some of the methodologies described above to explore a consistent way of estimating at same time celerities and velocities within the Weierbach experimental catchment in Luxembourg. A strategy to estimate celerity using hydrograph, soil moisture and water table response, and estimating velocity using tracers is presented, and coupled with the MIPs model at the 1-D scale.
3 VELOCITY AND Celerity DYNAMICS AT PLOT SCALE INFERRED FROM ARTIFICIAL TRACING EXPERIMENTS AND TIME-LAPSE ERT

ABSTRACT

The relationship between tracer velocities and wave or wetting front celerities is essential to understand water flowing from hillslopes to the stream. The connection between maximum velocity and celerities estimated by means of experimental techniques has not been explored. To assess the pattern of infiltrating water front and dominant flow direction, we performed sprinkling experiments at a trenched plot in the Weierbach catchment in Luxembourg. Maximum velocities and wetting front celerities were inferred at different depths using artificial tracers, soil moisture measurements (TDR), and geophysical techniques. The flow direction was predominantly vertical within the observed plot, with almost no lateral flow observed until depths of 2-3 m; shallow trench flow was intermittent and associated with preferential flow. Average celerity estimates using TDR and geophysical techniques were equal to 707 ± 234 mm h⁻¹ and 971 ± 625 mm h⁻¹, respectively. Vertical maximum velocity estimates were tracer-dependent and had very variable ranges: 109.3 ± 89.3 mm h⁻¹ (Cl⁻), 177.8 ± 199.1 mm h⁻¹ (Br⁻), and 604.1 ± 610.7 mm h⁻¹ (Li⁺). Preferential flow processes were inferred from maximum velocities apparently greater than celerities and scattered trench flow with highly variable tracer concentrations. The high variability between maximum velocities of different tracers indicated a complex pattern of tracer movement through the soil, not captured by celerity values alone. Our study demonstrated the importance to assess both velocities and celerities to understand flow dynamics in response to sprinkling while information on the wetting front alone would have missed important preferential flow processes.

Contribution: I was responsible for designing, implementing and executing the field experiment, collecting and analysing the data and writing. I partook in the MICS strategy application and the writing of sections 3.3.2 and 3.3.5.

3.1 INTRODUCTION

Spatial and temporal heterogeneity of soil and bedrock structure is known to control subsurface response, that often dominates runoff generation (Graham et al., 2010; McDonnell et al., 2007; Zehe and Sivapalan, 2009). Particularly in the unsaturated zone, the behaviour of the small-scale hydrological processes is highly nonlinear both temporally (wetting and drying phases) and spatially (Beven, 2012a). Despite its proven importance, many unknowns still need to be resolved to improve understanding of such heterogeneity, in terms of how it affects water travel time characteristics as well as hydrograph responses (Botter et al., 2010; Rinaldo et al., 2011).

Travel time distributions are controlled by water velocities and filled pore space (Rinaldo et al., 2011; Kirchner, 2016b). Conversely, the hydrograph response is controlled by celerities of the pressure responses and the effective storage that is filled and emptied as the wetting front progresses into the soil and the water tables rises and falls (Beven, 2010; McDonnell and Beven, 2014). One way to learn about the bulk effects of heterogeneities in the unsaturated zone at the hillslope and catchment scales is the interpretation of tracer observations to provide information about velocity distributions (Rinaldo et al., 2011) and simultaneous derivation of celerities from water content, piezometer and discharge responses (McDonnell and Beven 2014).

McDonnell and Beven (2014) recently stressed the importance of characterising both tracer velocities, the measure of how fast pore water moves, and celerities, the measure of how fast the storage of water responds to a perturbation, in response to a rainfall event. This is critical as it helps explain the old-water paradox where streams can respond quickly to rainfall inputs but with water that has resided in the catchment for weeks, months or years (Beven, 1989a; Kirchner, 2003). Beyond increased process understanding, the characterisation of velocities and celerities at the plot scale is necessary to implement physically reasonable model interpretations of flow at the larger hillslope and catchment scales.
Because of their nature, we expect velocity and celerity distributions to differ from each other, converging to similar values only in preferential flow domains (Hrachowitz et al., 2016). The differences between velocity and celerity are notions currently employed in the most novel modelling frameworks (Davies et al., 2011, 2013; Hrachowitz et al., 2013; Laine-Kaulio et al., 2014) and recent work showed the importance of experimentally derived tracer velocities in the spatial and temporal evolution of stream flow (Benettin et al., 2015; Bergstrom et al., 2016). Getting velocities and celerities right would mean that process representations are more likely to be, in the words of Kirchner (2006), right for the right reasons (see also Beven, 2010; McDonnell and Beven, 2014).

Sprinkling is the most widely used tool to control irrigation characteristics (Valipour, 2012; Valipour and Singh, 2016). In hydrological studies, sprinkling experiments carried out at trenched hillslopes are often used to characterise the vertical and lateral components of flow reaching different soil layers (McGlynn et al., 2002; Wienhöfer et al., 2009), allowing rainfall characteristics and, in part, boundary conditions to be controlled (McDonnell et al., 2007; Wienhöfer and Zehe, 2014). A recent sprinkling experiment showed the importance of the characterisation of multi-tracer approaches to estimate pore velocities, in an effort to characterise interflow and preferential flow (Jackson et al., 2016).

The observation of water flow is often combined with the detection of tracers, either natural, or artificial to quantify velocities. Chloride and bromide are amongst the most commonly used tracers to characterise water pathways (Graham and McDonnell, 2010; Perkins, 2011; Tyner et al., 2007). Bromide and lithium are considered to be near “ideal” tracers due to their very low natural abundance and relatively conservative characteristics (Flury and Papritz, 1993; Nickus, 2001). The interpretation of the tracer results may not, however, be simple. For example, suction lysimeters (Wagner, 1962) can be used to detect tracer arrival times (velocities) (Perkins et al., 2011), but the concentrations detected are expected to be a mix of mobile and relatively immobile water (Weihermüller et al., 2005). Additionally, geochemical processes, such as sorption/desorption, and root uptake effects will also affect measured concentrations (Weihermüller et al., 2007).
Soil moisture estimated using Time Domain Reflectometry (TDR) (Topp et al., 1980) can be used to detect the arrival of a wetting front (Haga et al., 2005), and some versions of the TDR probes can be used to infer electrical conductivity data as an indication of tracer arrival (Dalton et al., 1984; Persson, 1997). As wetting fronts can be highly spatially variable, obtaining spatially highly resolved data with point measurements using TDR remains challenging and expensive (Vereecken et al., 2014).

Electrical resistivity tomography (ERT) is a non-intrusive technique that can be used to provide spatially-resolved resistivity measurements of the subsurface (Loke and Barker, 1996; Dahlin, 2001; Binley and Kemna, 2005; Cassiani et al., 2006). Time-lapse surveys have been employed to characterise subsurface infiltration of water using the addition of tracers (Park, 1998; Slater et al., 2002; Cassiani et al., 2009), providing spatially and temporally resolved information on the wetting front.

The aim of this study is to explore the velocity and celerity responses at the plot scale, in a catchment where subsurface flows are known to contribute to riparian zone wetness and streamflows. Previous research in the Weierbach catchment has focused on identifying the dominant runoff generation processes (Fenicia et al., 2013; Wrede et al., 2015). Preliminary physiographic and geophysical investigations concluded that the fast drainage of the soil in addition to the relatively steep slopes generated lateral flow components in the subsurface and fractured bedrock (Wrede et al., 2015). However, the small-scale processes that are responsible for the hydrological response at catchment scale remain poorly understood.

Although the characterisation of velocities and celerities is important to infer flow pathways and residence times, how to best design experiments for this purpose is still poorly understood. This study examines downslope lateral flow in the soil profile (including preferential flow and patterns of local saturation), which previous experimental designs in the Weierbach catchment had not been able to track. Here, a three-fold monitoring protocol is designed for determining maximum velocity and celerity at plot scale. Installed on a trenched hillslope, the experimental set-up consists of (i) artificial tracers, (ii) time domain reflectrometry (TDR), and (iii) geophysical techniques. In the framework of controlled sprinkling experiments, the
complementarities and limitations of each of these techniques are explored – geared towards the estimation of maximum velocities and celerities within a schist plot.

3.2 DESCRIPTION OF THE EXPERIMENTAL FIELD SITE

The Weierbach, an experimental site located in the North-West of Luxembourg which has been monitored for its hydro-climatic response for more than 20 years. The catchment has an area of 0.45 Km² is predominantly forested, and it is underlain by Devonian slate. The altitude ranges from 422 to 512 m a.s.l.

Within this catchment, a 64 m² plot has been isolated and instrumented (Figure 5). The site is located on a north facing slope, on the left bank, just uphill of a forest road cut, 40 m from the river (Figure 5.a). The slope averages 10 degrees and is perpendicular to the stream. At this location, the regolith consists of three main layers, which developed from periglacial slope deposits on the fresh Devonian slate bedrock (Juilleret et al., 2011, 2016).

The soil is classified as a Dystric Endoskeletic Cambisol (Colluvic, Bathyruptic, Siltic) in the WRB (IUSS Working Group WRB, 2015). From 0 to 40 cm depth, the soil has developed from a loamy material originated from periglacial slope deposits. It is divided in an upper thin organic rich A horizon (0 to 8 cm depth) and a cambic B horizon (8 to 40 cm depth). From 40 to 110 cm, the C horizon is composed of periglacial deposits dominated by slate rock fragments. At about 110 cm a lithic discontinuity occurs, separating the upper periglacial cover bed from the slate rock substratum. The deeper layer, from 110 to 500 cm depth, is constituted of weathered and fractured slate. The nearly vertical fractures, which are gradually closing with depth, permit rooting and, despite the impervious properties of the slate lithology, water can infiltrate through it. According to (Martínez-Carreras et al., 2016), the mean drainage porosity decreases from the soil surface to the regolith-bedrock interface: 75%, 65% and <9% for the A, B and C horizons, respectively.
3.3 MATERIALS AND METHODS

3.3.1 The sprinkling experiments

Celerity and velocity depend on input intensity and antecedent conditions (Beven, 2012a). Two sprinkling experiments were conducted under similar conditions of wetness. Intensity rates were kept as homogeneous as possible, in order to estimate maximum velocities and celerities and under comparable conditions.
3.3.1.1 Site implementation

Two garden sprinklers Gardena AquazoomTM 250/2 were used to perform artificial rainfall experiments, with the objective to apply water as uniformly as possible onto the plot surface. Rainfall intensities and uniformity were assessed by two types of water collectors. Permanent rainfall collectors were placed at 9 locations within the plot (Figure 5.b). During the sprinkling, 7 additional rainfall collectors were used to characterise more accurately the uniformity of the sprinkled water on the surface. Rainfall was measured at hourly time steps during the experiments. Rainfall intensities were derived from the spatial averaged value of the collectors. A summary of the sprinkling experiments is shown in Table 1.

Table 1. Summary of irrigation for Experiment 1 and Experiment 2. Information of times (dates, number of sprinkled days), antecedent conditions (API=antecedent precipitation index, calculated for a 30 and 7 days period before the experiment (in brackets); AMC = antecedent moisture conditions, at two depths in the soil); total irrigation (mm) measured over an area of 64 m²; quantity of tracers applied.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dates</td>
<td>31/03-10/04/2014</td>
<td>11-16/03/2015</td>
</tr>
<tr>
<td>Days of sprinkling</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td>API 30 [7] (mm)</td>
<td>12 [0.9]</td>
<td>50 [8]</td>
</tr>
<tr>
<td>AMC 10 cm depth (cm³ cm⁻³)</td>
<td>0.23</td>
<td>0.27</td>
</tr>
<tr>
<td>AMC 50-80 cm depth (cm³ cm⁻³)</td>
<td>0.40</td>
<td>0.35</td>
</tr>
<tr>
<td>Total irrigation (mm)</td>
<td>573.3</td>
<td>352.9</td>
</tr>
<tr>
<td>Tracers applied (kg) [g L⁻¹]</td>
<td>NaCl 25 [5]</td>
<td>5 [5]</td>
</tr>
<tr>
<td></td>
<td>KBr 5 [2.5]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LiCl</td>
<td>2.5 [1]</td>
</tr>
</tbody>
</table>

The stream water of the Weierbach was used for the irrigation of the plot. This water presents a low mineralization level (EC about 50 µS cm⁻¹) and its chemical composition did not interfere with the artificial tracing experiments. The natural background concentration of the tracers used during the experiment was estimated using data collected bi-weekly over a three year period (2011-2013) before the two experiments.

TDR sensors were used to measure the soil volumetric water content (VWC), before, during and after the sprinkling events. Changes in soil moisture and
movements of the wetting front were estimated with 5 water content reflectometers (WCR – CS616, Campbell Scientific, 2011 Ltd.). The sensors were installed horizontally at 10 cm depth and vertically between 50 and 80 cm depth (Figure 6). Additionally, a multi-parameter WCR sensor (CS650, Campbell Scientifics Ltd.) was installed vertically at the middle of the plot at 50 to 80 cm depth. It recorded electrical conductivity (EC) and soil VWC. All sensors were connected to a CR10X datalogger (Campbell Scientifics Ltd.) for continuously recording soil VWC, temperature and EC at 15 min intervals.

Figure 6. Description of the experimental equipment. In the box, view of the WCR, temperature probes and porous cup inserted horizontally at 10 cm depth and vertically between 50 and 80 cm depth in each of the three soil pits (S1, S2 and S3). The trench position, including the three gutters (T1, T2, T3) is shown in orange.

Suction lysimeters (PTFE/Quartz – SDEC France) were inserted horizontally at 10 cm depth or vertically below the deeper WCR, at a depth of 80 to 90 cm. The suction lysimeters allowed the soil solution that drained the soil during the infiltration experiments to be sampled at variable time step (between 30 minutes and 3 h) in order to determine the evolution of the artificial tracer concentrations.

In order to collect shallow subsurface water flow, a 350 cm long trench was excavated at the downstream part of the experimental site (Figure 5.a). Through the
trench, 3 lateral flow troughs of 150 cm length were inserted. They were used to conduct the outflow from the trench at 25, 50 and 130 cm depth to collection points, equipped with a volume collector and a tipping bucket rain gauge (Model 52203, Young). The number of tips recorded by the tipping buckets was then converted to volume of shallow lateral flow at a 5 min time step. The sensors were connected to a DRX10 datalogger (Campbell Scientitics Ltd.).

In order to capture deeper lateral flow, two wells were installed at the base of the trench. The drilling was performed from the surface of the forest road, on the two sides of the roof covering the base of the plot. The two wells were drilled at 2 and 2.4 m depth and went through the fractured slate layer. Both wells were equipped with OTT Thalimedes probes to measure water height, temperature and EC at 1 min time step.

### 3.3.1.2 Sprinkling experiment 1

The goal of the sprinkling experiment was to generate heavy rainfall conditions, which would trigger lateral flow. The first sprinkling experiment was conducted in two steps between the 31st March and 10th April 2014 separated by a two days period (April 05th and 06th) without sprinkling. Meteorological conditions prior to the experiment were relatively dry: the antecedent precipitation index (API) was equal to 12 mm for a 30 days period before the experiment (API30) and 0.9 mm for a period of one week prior the experiment (API7) (Table 1). The antecedent moisture content, calculated as the mean daily value of the WCR probes, was 0.23 cm$^3$ cm$^{-3}$ at 10 cm depth and 0.40 cm$^3$ cm$^{-3}$ at 50 to 80 cm depth. During step 1, only one sprinkler was used and mean intensities ranged from 7.6 to 11.4 mm h$^{-1}$, depending on wind and cleanliness of the sprinkling system. Since no trench flow was measured, a second sprinkler was used during step 2 and contributed to rise the applied intensity up to 20.5 mm h$^{-1}$ (Table 2). The total rainfall volume sprinkled over the first experiment was equivalent to 573 mm (a total of 36700 L).

During the sprinkling experiment, on Day 3 and Day 8 (April 2nd and 9th – Table 1), a tracer solution of respectively 3000 and 2000 L with 5 g L$^{-1}$ NaCl was used to
sprinkle the area. On Day 9 (April 10th), a solution of 2000 L with 2.5 g L\(^{-1}\) KBr was applied.

The first NaCl application (Day 3) had as primary objective the assessment of the wetting front with time-lapse ERT in combination with the *in situ* probes, ultimately needed to measure celerity response. Adding tracer to the sprinkled water was necessary to estimate maximum velocities by detecting the tracer arrival from the chemical composition of sampled water at each measurement point. The *in situ* probes could characterise point-based celerity information for each sprinkling day.

The later applications had the objective of characterising the movement of water through the soil with different tracers, to account for their differences.

Table 2. Sprinkling rates according to the sprinkling set-up: (a) Experiment 1, step 1, using one sprinkler; (b) Experiment 1, step 2, using 2 sprinklers; (c) Experiment 2, using 2 sprinklers. Total rainfall, Total time sprinkling and mean intensity are shown. **Bold**: days of artificial tracer application.

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<th>Mean intensity</th>
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3.3.1.3 Sprinkling experiment 2

Experiment 2 (Table 1) was conducted in March 2015, in order to replicate the wetting phase and using a new salt, LiCl. The sampling interval for the suction lysimeters was reduced up to 1h to give a better definition of the evolution of the artificial tracer concentrations.

In terms of antecedent conditions, API30 was equal to 50 mm (API7=8 mm), about 4 times higher than in Experiment 1. The average VWC was 0.27 cm$^3$ cm$^{-3}$ at 10 cm depth and 0.35 cm$^3$ cm$^{-3}$ at 50-80 cm depth respectively, and did not differ significantly from Experiment 1. The hillslope was sprinkled with intensities as similar as possible to Experiment 1 (part 2) for a total of 6 days, with a total irrigation of 353 mm (equal to 22600 L). Two tracers were applied on Day 3 of Experiment 2 (13/03/2015): a solution of 1000 L containing 5 g L$^{-1}$ NaCl and one of 1000 L containing 1 g L$^{-1}$ LiCl were used. NaCl was employed again in order to compare estimates of celerities of Experiment 1 and 2 using the same tracer.

3.3.1.4 Chemical analyses of tracers in the soil

During both experiments, soil solution samples were taken (i) using the suction lysimeters at 6 different locations in the soil and (ii) at the volume collectors placed at each trough exit (Figure 6). All collected water samples were filtered at 0.45 µm using Acrodisc syringe filters (Pall Corporation) before analysis of EC, chloride (Cl$^-$), bromide (Br$^-$) and lithium (Li$^+$) concentrations. The concentrations were analysed using ionic chromatography (Dionex ICS-5000). The detection limit of the analyses was 0.01 mg L$^{-1}$ for Cl$^-$, 0.02 mg L$^{-1}$ for Br$^-$ and Li$^+$. Tracer recovery at the trench face was calculated with input-output rate estimation. For each collected sample from the suction lysimeters and trench, the quantity of tracer with respect to the input concentration (respectively equal to 6.3 g L$^{-1}$ for Cl$^-$, 5.2 g L$^{-1}$ for Br$^-$, 0.3 g L$^{-1}$ for Li$^+$) was also calculated.

EC measured with the multi-parameter WCR sensor is widely employed as a proxy value for ion concentration (as largely used in field studies, see McNeil and Cox, 2000; Siosemarde et al., 2010). Since different tracers were employed, a
correlation equation between EC and the tracers could not be generated, but the EC trend was used to assess tracer dynamics at that location.

### 3.3.2 Monitoring infiltration using time-lapse ERT

The ERT method is widely described in the geophysics literature and used to study subsurface variations in electrical resistivity linked with variation of water content, clay content, porosity, saturation and the concentration of dissolved electrolytes (Telford et al., 1990; Loke and Barker, 1996; Tsourlos and Ogilvy, 1999; Dahlin, 2001). Compared to standard ERT, time-lapse ERT can provide information on the time variability of electrical resistivity. Time-lapse ERT monitoring involves performing identical ERT surveys several times at the same location (Daily et al., 1992), for example before, during and after the sprinkling experiment. Salt tracer injection implies an increase in electrical conductivity and consequently a corresponding decrease in electrical resistivity. Time-lapse surveys demonstrated the high potential for monitoring water infiltration during rain experiments (Descloitres et al., 2008; Travelletti et al., 2012).

However, two main limitations of the ERT method can be identified: (i) the non-uniqueness of the inversion process, meaning that multiple spatial reconstructions of the resistivity may be consistent with the observations, and (ii) the smoothness-constrained regularisation method, which tends to smooth the resistivity models creating difficulties to locate the infiltration front precisely. To overcome these issues, several strategies for ERT interface detection have been developed (Nguyen et al., 2005; Chambers et al., 2014; Ward et al., 2014). In another study, Audebert et al. (2014) developed the multiple inversions and clustering strategy (MICS) to better delineate the infiltration area on time-lapse ERT monitoring data sets. The methodology was assessed on numerical data and leachate recirculation field data. For the first time, this methodology was used in a hydrological study, in order to delineate the infiltration at the plot scale.

#### 3.3.2.1 ERT transect

The ERT transect used in this experiment features 120 electrodes with an electrode spacing of 0.5 m. The ERT survey location is represented by a blue line in
Figure 5. The alignment of the electrodes follows the direction of the main slope gradient and the centre of the electrode line was located just above the upper limit of the sprinkling area. Precise location of each electrode was determined using a Trimble DR3300 Total station. The ERT measurements during tracer injection experiments were conducted with a Syscal Pro 120 (ten-channel) resistivity meter from IRIS instruments. A Wenner-Schlumberger quadripole array configuration was used for the measurements due to its good depth of investigation and spatial resolution (Dahlin and Zhou, 2004; Athanasiou et al., 2007).

3.3.2.2 The multiple inversions and clustering strategy (MICS)

The MICS methodology is based on two steps:

i. A multiple inversion step to take into account the variability of the inversion process in varying inversion parameters. In this paper, inversions of time-lapse ERT data sets were performed to reconstruct the resistivity distributions using the Boundless Electrical Resistivity Tomography code (BERT) from Günther et al., (2006). To determine the misfit between simulated and field data sets of apparent resistivity, the classical inversion tools use the root mean square error (RMSE) (Loke and Barker, 1996) and the Chi² mathematical criteria (Günther et al., 2006). The resistivity models exhibiting a RMS higher than 5% were discarded.

ii. A clustering strategy, based on a grouping criteria, to classify the results in delineating the infiltration area on the final profile (Audebert et al., 2014). In the original paper Audebert et al. (2014), the grouping criteria was based on the following rule: if a mesh cell belongs to the infiltration area for all clustering profiles (100% of belonging), this cell belongs to the infiltration area in the final profile. This stringent criterion of 100% would allow greater confidence in the delimitation of the area of infiltration, however retaining part of the information. This criterion was therefore relaxed and the % of times that each mesh element belonged to the infiltration area was computed using 4 grouping criteria with 60%, 70%, 80%, 90% belonging thresholds.
On the basis of previous MICS numerical tests (Audebert et al., 2014), a total of 32 inversions is required for each resistivity data set. Sensitivity was computed for each inversion parameter set and data interpretation limited to the smallest high-sensitivity area among all the inversion results (Audebert et al., 2014). The MICS methodology was applied to the four ERT data sets recorded before and during the tracer injection experiment, requiring a total of 128 inversions.

3.3.3 Estimating celerity and maximum velocity from the sprinkling experiments

Figure 7 shows a conceptual illustration of the response of a 1-D non-confined system to a water input. Figure 7.a shows the traced water input. The water input creates a wetting front moving in the vertical direction, which displaces some of the particles of water already stored in the soil (Figure 7.b). In such system, the maximum velocity is defined as the fastest direct movement of the tracer. There is an expectation that the wetting front response will be faster than the tracer responses as a result of the celerity being faster than the water velocity (Figure 7.c1). On some occasions, bypassing or preferential flow might occur, limited by the speed of the fastest (maximum) velocity. Only in this case, where tracer moves ahead of the main wetting front, will the maximum velocity therefore appear as higher than the wetting front (CELERITY) (Figure 7.c2). For the maximum velocity to be higher, tracer would need to be detected in the suction lysimeters (sampled at smaller intervals) before detecting any change in the moisture content, either due to preferential flow missing the TDR probe or within the uncertainty of MICS.

The celerity was calculated for each sprinkling day using the time of the first response of VWC and trench flows to sprinkling, respectively measured by TDR probes and tipping buckets. The overall response of the plot was described by showing a range of values, due to the time-range of the measurements. The celerity of the wave response was estimated dividing the depth of the probe by the lag time between start of irrigation and response of the probe. The probes inserted vertically in the hand dug soil pits are expected to respond as soon as the upper part of the probe is wetted. The values of celerity for the deep probes were calculated as a range from minimum (50 cm depth) to average depth of the probe (65 cm depth).
Figure 7. One-dimensional sketch of a schematic soil box showing the difference between celerity and velocity estimated in this paper. The response to the sprinkling event using traced water (a) is shown. A wetting front is generated as a consequence to the pressure given by the water input (b). A process of displacement moves the water stored in the soil until reaching the measurement point (c1). Bypassing flow occurs when traced water moves through preferential flow reaching the measurement point in correspondence with, or even “before”, the wetting front (c2).

The maximum velocity was calculated using the artificial tracer concentrations measured in the soil water samples collected in the suction lysimeters, and from the arrival time of the tracers at the trench face. In case of the suction lysimeters, the values are given as ranges due to the coarser sampling interval (Section 3.3.1.1). In the case of the suction lysimeters inserted vertically in the hand dug soil pits, the deep probes, the values of maximum velocity were calculated over the average depth of the probe (85 cm depth). The timing of the sharp rise in concentration following the addition of tracer provides the estimate of maximum velocity, but might miss any preferential flow occurring in between sampling time-steps.
The maximum velocities estimated for the sprinkling days were directly compared with the correspondent celerities for the same days.

3.3.4 Estimating celerity from MICS

Wetting front celerities were calculated from the depths of the infiltration delimited with MICS and for each of the 4 grouping criteria (Section 3.3.2.2). Celerities were computed considering the topographic position of the three VWC profiles (positions corresponding to S1, S2 and S3 in Figure 6) at different times. MICS celerity was computed at the correspondent location in the ERT profile. The maximum depth reached is divided by the elapsed time, corresponding to the time interval of the three ERT data sets, recorded respectively 70, 175 and 280 min after start of salt sprinkling.

3.3.5 Estimating apparent porosity

The ratio between the injected volume of water and the infiltration volume delimited by MICS at each time step, $\varepsilon_a$, defined as “apparent porosity” by Clément et al. (2011) and Audebert et al. (2016), provides an estimate of the pore volume used for water flow. In the first part of their study, Audebert et al. (2016) showed that a small value of $\varepsilon_a$ (between 3 and 9%) implies that a very small fraction of the pore volume is available for water flow, which could be interpreted as fast and possibly preferential flow pathways.

3.4 RESULTS

3.4.1 Trench flow and velocity/celerity estimates

During Experiment 1, the relative amount of lateral flow reaching the trench, was a total of only 24 L, equivalent of a 0.03% of the total input sprinkled onto the experimental plot surface. The lateral connectivity, i.e. trench flow, was reached only on the last 3 sprinkling days of Experiment 1. A larger precipitation rate than initially applied (on average between 15 and 28 mm h$^{-1}$) was necessary to generate lateral connectivity and initiate trench flow. Cl$^-$ was used in 3 different occasions, and its interpretation in terms of response at the trench face is complicated due to the non-
activation of the trench during the first part of Experiment 1. Therefore, Cl⁻ data were not included in the analysis.

On Day 9, April 10th, T1 and T2 were activated by water sprinkled prior to the salt experiment, with estimated celerity of respectively 1000, 166 and 90 mm h⁻¹. Before applying the KBr solution, the flow at T1 and T2 slowed down due to a 20 min break in the irrigation. Only after 20 min of sprinkling the salt solution, both T1 and T2 flow increased again, allowing a second estimate of celerity to be made of respectively 750 and 1500 mm h⁻¹ (Table 3.a). At T3, the first tip was recorded 4 hours after starting sprinkling on that day, and one hour after starting the tracing experiment (celerity of 1733 mm h⁻¹).

Similar results were observed during Experiment 2: only a total of 30 L flowed to the trench (0.08%), even though the trench was activated on each sprinkling day. During Experiment 2 (March 13th 2015), only T1 was activated with celerity of 63 mm h⁻¹. Sprinkling was continuous, but before sprinkling Li⁺, filters were cleaned, and consequently the intensity was increased. Water reached T2 (with a celerity of 1000 mm h⁻¹), before T1 reactivation (celerity of 273 mm h⁻¹), see Table 3.b).

The maximum velocities at the trench were estimated using the detection time of the applied tracers. During Experiment 1, Cl⁻ concentrations ranged between 9.30 and 1113.80 mg L⁻¹ (T1), between 13.20 and 598.90 mg L⁻¹ (T2), and between 4.20 and 260.90 mg L⁻¹ (T3). Br⁻ concentrations ranged between 118.50 and 556.00 mg L⁻¹ (T1), between 5.00 and 176.00 mg L⁻¹ (T2), and between 0.50 and 133.00 mg L⁻¹ (T3). Br⁻ reached T1 25 min after starting the tracer experiment and T2 after only 15 min (maximum velocities of respectively 600 and 1200 mm h⁻¹). During Experiment 2 Cl⁻ concentrations ranged between 6.00 and 96.00 mg L⁻¹ (T1), and between 7.80 and 242.50 mg L⁻¹ (T2). Li⁺ concentrations ranged between 0.20 and 2.40 (T1) and were only equal to 0.02 mg L⁻¹ (detection limit) in T2. On March 13th, 2015, Li⁺ reached T1 30 min after start of sprinkling (maximum velocity of 517 mm h⁻¹) while it reached T2 only on the next day (maximum velocity of 17 mm h⁻¹). The chemical analysis on the volumes collected at the trench during Experiment 2 revealed that Br⁻ concentrations (used as tracer only during Experiment 1, see Table 1) were still high nearly one year later (0.70 - 30.00 mg L⁻¹ Br for T1, 8.00 - 273.10 mg L⁻¹ for T2).
Table 3. Celerities (a) and velocities (b) estimated at the trench expressed as mm h\(^{-1}\). Each value of velocity refers to the detection of the tracers in the sampled water. Cl\(^-\) data are not included because of the difficulty in the interpretation. X = no data, meaning that there was no trench flow. Underlined: no data on that day - tracer reached on the next day.

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<td>Li(^+)</td>
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3.4.2 Chemical evolution of soil water

Figure 8 shows the time series of rainfall (Figure 8.a) and the multi-parameter probe placed in S2 at 50-80 cm depth (Figure 8.b). Both VWC and EC values (expressed as µS cm\(^{-1}\)) are shown, respectively in green and orange. The time series of EC monitored by the sensor in the soil matrix is characterised by 3 phases (Figure 8.b). The data recorded after Experiment 1 show peaks of EC correspondent to the peaks of VWC during rainfall events (Figure 8.b, Part 1). The higher value of EC during these peaks corresponds to 118.4 µS cm\(^{-1}\), likely to be much higher right after Experiment 1. The magnitude of these peaks got progressively smaller in the last part of 2014, until almost no fluctuation was present in early 2015 (Figure 8.b, Part 2). During Experiment 2, EC started with the lowest value of 21.5 µS cm\(^{-1}\) and raised again with the salt tracing, responding to the sprinkling with 15 min lag (one time step) with respect to the VWC probe (Figure 8.b, Part 3, and Figure 8.d). The magnitude of Experiment 2 peak had a maximum of 98.5 µS cm\(^{-1}\).
Figure 8. Time series of (a) rainfall, (b) soil moisture, expressed as volumetric water content (VWC, green) and electrical conductivity (EC, orange) at the deep probe in S2. Three main periods are distinguished: (1) remobilization of the salt during natural rainfall events; (2) dilution of salt during natural rainfall events and (3) the effect of Experiment 2 on EC due to raise in salt concentration. Graphs (c) and (d) correspond to a zoom of period 3 and show the sprinkling sequence, VWC and EC response during Experiment 2. On Day 3, the EC rises again due to the salt solution sprinkled.
Before Experiment 1, background EC of the soil water collected in the suction lysimeters at 85 cm depth was 152 µS cm\(^{-1}\). The average background Cl\(^-\) value in the suction lysimeters was 3.23 ± 2.24 mg L\(^{-1}\) (no Br\(^-\) or Li\(^+\) were detected in the samples). NaCl and KBr input water had EC values respectively of 9500 and 2300 µS cm\(^{-1}\). During Experiment 1, EC in the water extracted from the lysimeters at 85 cm depth raised up to 1400 µS cm\(^{-1}\). The samples collected using the suction lysimeters at 10 cm depth had concentrations of Cl\(^-\) up to 16.1% higher than those placed at 85 cm depth, and concentrations of Br\(^-\) up to 9.1% higher. Before Experiment 2, both Cl\(^-\) and Br\(^-\) concentrations were still high with respect to the initial background concentrations: 12.87 ± 5.18 mg L\(^{-1}\) for Cl\(^-\), 7.48 ± 9.90 mg L\(^{-1}\) for Br\(^-\) at 10 cm depth, 64.85 ± 31.48 mg L\(^{-1}\) for Cl\(^-\) and 31.60 ± 19.75 mg L\(^{-1}\) for Br\(^-\) at 85 cm depth. During the first days of sprinkling, no peaks in EC were recorded in the soil matrix (Figure 8.d). With Experiment 2, NaCl and LiCl input water had values of EC respectively of 9500 and 2600 µS cm\(^{-1}\).

The tracer concentrations for each suction lysimeter, during both Experiment 1 (left graphs) and Experiment 2 (right graphs), are shown as box plots in Figure 9. The full concentration range over the totality of the sprinkling days is shown for each of the suction lysimeters, with red lines indicating the median value. On the first days of Experiment 2, before applying tracers, average concentrations on the plot were 37.00 mg L\(^{-1}\) Cl\(^-\) and 39.00 mg L\(^{-1}\) Br\(^-\) at 10 cm depth, 52.00 mg L\(^{-1}\) Cl\(^-\) and 28.00 mg L\(^{-1}\) Br\(^-\) at 85 cm depth. During Experiment 2, Cl\(^-\) concentrations in the suction lysimeters ranged between 8.20 and 770.00 mg L\(^{-1}\). Li\(^+\), sprinkled on March 13\(^{th}\), was detected in all the suction lysimeters, and its concentration ranged between 0.03 and 18.40 mg L\(^{-1}\). Concentrations at 10 cm depth were up to 3.6% higher than 85 cm depth for Cl\(^-\), and 0.2% for Li\(^+\). During Experiment 2, Br\(^-\) was still detected at all locations. Its concentrations were very similar at both depths and ranged between 0.30 and 58.00 mg L\(^{-1}\) (Figure 9).
3.4.3 Maximum velocity estimates

Figure 10 shows estimates of maximum velocities calculated for the application of each tracer: April 02 (Cl\textsuperscript{−}) and 10 (Br\textsuperscript{−}), 2014 and March 13, 2015 (Cl\textsuperscript{−} and Li\textsuperscript{+}). Maximum velocities were always higher in the deeper probes on average by 4.0 ±5.4% (Figure 10). Cl\textsuperscript{−} maximum velocities were very similar in Experiment 1 and 2,
with an average value of $36 \pm 16$ mm h$^{-1}$ (shallow probes) and $127 \pm 65$ mm h$^{-1}$ (deep probes) in Experiment 1 and $38 \pm 14$ mm h$^{-1}$ (shallow probes) and $123 \pm 87$ mm h$^{-1}$ (deep probes) in Experiment 2 (Figure 10).

Even though Cl$^-$ and Li$^+$ were applied on the same day during Experiment 2, their values of velocity were very different. Li$^+$ had the highest estimates of maximum velocity (Figure 10): on March 13$^{th}$, in S3 Li$^+$ reached the deep probe before the shallow probe at the same location, and almost simultaneously with the shallow probe of S2 and deep probe at location S1. Concurrently, maximum velocities were respectively $1282 \pm 351$ mm h$^{-1}$ for deep probe S3 and $1260 \pm 191$ mm h$^{-1}$ for deep probe S1 (Figure 10). Li$^+$ reached deep S2 only on the overnight sample. Average Li$^+$ maximum velocities were $103 \pm 68$ mm h$^{-1}$ and $677 \pm 420$ mm h$^{-1}$ respectively for shallow and deep probes.

![Figure 10](image.png)

Figure 10. Range of maximum velocities (y axis) estimated from tracer concentrations at position S1 (yellow), S2 (violet) and S3 (light blue), expressed as mm h$^{-1}$. Each value is expressed as a range and refers to the detection of the tracers in the sampled water. The node, squared for 2014 samples and round for 2015 samples, indicates the average value.

On April 10, Br$^-$ was detected only in S3 (Figure 10, blue) only 3 to 5 h after sprinkling, with maximum velocities of respectively $27 \pm 10$ mm h$^{-1}$ (shallow probe)
and 232 ±83 mm h⁻¹ (deep probe), but was detected in S1 and S2 only after a 2 days-long delay (data not shown). On Experiment 2, Br⁻ was present in all the suction lysimeters at all times and progressively diluted and was therefore not used for velocity calculations.

### 3.4.4 Celerity estimates

The estimates of celerity could be calculated from the VWC data. Averaged VWC for the three locations at same depth within the hillslope (S1, S2 and S3), plotted against the rainfall, are shown in Figure 11. Figure 11.a presents both natural (in black) and sprinkled rainfall (in blue), expressed as mm/15 min. Figure 11.b shows the time series of VWC for both shallow (orange) and deep (green) probes. Over the full time series, at 10 cm depth, the VWC ranged between 0.709 and 0.185 cm³ cm⁻³, while at 65 cm depth it ranged between 0.516 and 0.351 cm³ cm⁻³, showing higher fluctuations in the shallow probes. Correlation between the probes (calculated for the full time series and only between probes at same depth) ranged between 0.80 and 0.89. Even if the API was higher before Experiment 2 by 38 mm (API30), the average VWC was higher before Experiment 1 by 5%.

![Figure 11](image.png)

Figure 11. (a) Time series of rainfall for the period March 2014 – May 2015 including the 2 experimental periods. (b) Time series of averaged VWC, for shallow and deep probes.
Figure 12 shows estimates of celerities at the plot scale calculated for the application of each tracer: April 02 (Cl\(^-\)) and 10 (Br\(^-\)), 2014 and March 13, 2015 (Cl\(^-\) and Li\(^+\)). Celerity values were always higher in the deep probes on average by 5.1 ±2.3% (calculated from Figure 12). Averaged values of celerities in Experiment 1 were respectively 420 ±197 mm h\(^{-1}\) (shallow probes) and 747 ±379 mm h\(^{-1}\) (deep probes) for April 02, and 579 ±488 mm h\(^{-1}\) (shallow probes) and 1183 ±448 mm h\(^{-1}\) (deep probes) for April 10 (Figure 12). During Experiment 2, on March 13\(^{th}\) 2015, celerities were significantly lower showing that at all locations water needed more time to reach the measurement points. Average celerities were respectively 84 ±13 mm h\(^{-1}\) for shallow probes and 384 ±85 mm h\(^{-1}\) for deep probes (Figure 12).

![Figure 12. Celerities estimated from VWC data expressed as mm h\(^{-1}\). Each value of celerity refers to the start of response in terms of VWC at each location. For each day, the values on the left refer to the shallow probes, while the values on the right refer to the deep probes.](image)

### 3.4.5 Time-lapse ERT

This section focuses on Day 3 of Experiment 1, April 2\(^{nd}\), when the NaCl solution was sprinkled for the first time. Figure 13 shows the time series of sprinkled rainfall (a) and VWC responses (b). The plot was sprinkled for 1.5h (from 10 h 35 min to 12 h, indicated by P1 in Figure 13.a). After a stop of 2.5h, the plot was sprinkled with the NaCl solution (P2, orange-coloured). The three time steps of time-lapse ERT following
salt sprinkling are indicated by grey vertical lines: time steps b, c, and d (70, 175 and 280 min after the beginning of salt sprinkling, respectively).

Figure 13. Time series of artificial rainfall (a) and averaged value of VWC response (b) on Day 3 of Experiment 1. Vertical lines show the time step of the time-lapse ERT profiles that followed the start of sprinkling of the salt solution. In grey, letters indicate the time step corresponding to Figure 14.

3.4.5.1 Resistivity changes due to salt application

Figure 14 presents the ERT results obtained during Experiment 1 of salt sprinkling. Profile (a) represents the initial interpreted resistivity (before the beginning of the salt sprinkling) and was obtained from a standard inversion procedure (i.e. L1-norm, \( w_z \) equal to 1 and a \( \lambda \) value of 20). The variability of resistivity with depth corresponds well with the regolith vertical structure as observed in the trench and the core drillings of both wells. Resistivity in the first 0.5 m depth (A and B horizons) is around 1000 \( \Omega \) m (light blue, Figure 14.a). Between 0.5 and about 2.0-2.5 m depth, resistivity forms a sharp peak (yellow to red, Figure 14.a), with a maximum of 7000-10000 \( \Omega \) m at around 1.0-1.5 m depth. The increase in resistivity corresponds to the C horizon, whilst the decrease deeper in the profile corresponds to the first heavily fractured part of the bedrock. Resistivity progressively decreases to a minimum of 100-500 \( \Omega \) m at 5 m depth, as bedrock becomes fresher (dark blue, Figure 14.a). The pre-sprinkling signal is therefore
characterised by very low porosity and resistivity at deeper layers, due to the
physical properties of the bedrock.

The values of resistivity obtained with the standard inversion of the initial ERT
data set ensures that the resistivity contrast between the salt tracer solution used
during Experiment 1 (conductivity of 9.5 mS cm\(^{-1}\), corresponding to a resistivity of 1.1
Ω m) and the surrounding medium, will be high (particularly until 2.5 m depth where
pre-sprinkling resistivity is high).

![Figure 14](image)

**Figure 14.** (a) Results of a standard inversion of the initial time step before salt sprinkling experiment. (b, c and d) Visualisation of the results of the MICS strategy applied to the three
time steps following the starting of the tracer experiment, respectively 70, 175 and 280 min
after start of salt sprinkling. The infiltration bulb at each time step is characterised by blue to
white-coloured pixels for the 100% to 60% grouping criterion. Grey-coloured areas
correspond to criteria lower than 60%.

### 3.4.5.2 Using MICS to characterise water penetration depth

MICS results are presented according to grouping criteria between 30 and 100%
(Figure 14.b, c and d). Each grouping criteria result is shown based on the colour
ramp – from grey for areas that changed less than 60% of the times, to white, for intermediate values, and blue, assigned to the clustering result indicating the pixels that were changing in all the 32 inversions for each time step (100%). An infiltration plume based on the grouping criterion is therefore visible. In the upper part of the plot (S3), the plume of infiltration reaches 1.6 m (90%) to 2.25 m depth (70%) depending on the grouping criterion (Figure 14.b). The tracer infiltration expands in depth in the middle (S2) part of the plot (until 1.00 to 1.60 m) and partially in the downslope direction (Figure 14.c). Only on the third time step (Figure 14.d) does the plume reach a depth of 1.35 to 1.85 m in the bottom part of the plot (S1). The maximum depth is reached at location S3, with 1.95 m (90%) to 2.45 m depth (70%). No significant resistivity changes indicating infiltration are observable below 2.5 m.

### 3.4.5.3 Celerity estimated with MICS

Celerity responses on 02/04/2014, using both deep VWC values and MICS values estimated using different grouping criteria, are shown in Table 4. In both VWC and MICS estimates the lower part of the plot (S1) has lower estimates of celerity than the middle (S2) and top part (S3) (Table 4). The averaged values for MICS are $1761 \pm 281$ (S3), $986 \pm 215$ (S2), and $257 \pm 172$ (S1) mm h$^{-1}$. VWC-derived average estimates of celerities are $921 \pm 76$ (S3), $788 \pm 112$ (S2) and $412 \pm 30$ mm h$^{-1}$ (S1). VWC-derived estimates show slower celerities with respect to MICS-derived estimates in the case of the top (S3) and middle (S2) locations (Table 4). The bottom site (S1) has an opposite pattern: MICS estimates are lower than VWC ones.

Table 4. Celerities estimated using the VWC data and the correspondent celerity estimated using MICS. **Bold:** average values. All the estimates are expressed in mm h$^{-1}$.

<table>
<thead>
<tr>
<th>Position</th>
<th>VWC 70%</th>
<th>VWC 80%</th>
<th>VWC 90%</th>
<th>MICS Average</th>
<th>MICS 70%</th>
<th>MICS 80%</th>
<th>MICS 90%</th>
<th>MICS Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>S3</td>
<td>921 ±76</td>
<td>1929</td>
<td>1714</td>
<td>1371</td>
<td>1671 ±281</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>788 ±112</td>
<td>1200</td>
<td>986</td>
<td>771</td>
<td>986 ±215</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>412 ±30</td>
<td>429</td>
<td>257</td>
<td>86</td>
<td>257 ±172</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>707 ±234</td>
<td></td>
<td></td>
<td>971 ±625</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.4.5.4 Change in water filled porosity

The apparent porosity was calculated at the three time steps following the tracer injection and for each grouping criteria. The lower range of porosities observed for time step (b) is between 1.6% (60% criterion) and 4.7% for the 100% criterion. Time step (c) ranges between 3.3% (60% criterion) and 12.0% (the maximum value, for 100%) and time step (d) has intermediate values, between 3.4% (60%) and 10.4 (100%). Only one value exceeded 10%. In the same event, the VWC increment was on average 5.7% at 65 cm depth. Taking into account all the sprinkling days of both experiments, the VWC increment was on average 44.9% at 10 cm depth and 7.9% at 65 cm depth.

3.5 DISCUSSION

3.5.1 A predominantly vertical flux direction

It is known from other studies in the Weierbach catchment that subsurface lateral flows contribute to seepage into the riparian areas (Martínez-Carreras et al., 2015; Wrede et al., 2015). The flows on the experimental plot, just 40 m from the stream were, however, predominantly vertical, even after applying large amounts of water. In fact, low volumes of flow reached the trench during the experiments (respectively 0.03% in Experiment 1 and 0.08% in Experiment 2), meaning that most of the water was infiltrating to deeper layers. The near absence of lateral flow during both experiments indicated a strong vertical flow preference. This was consistent over all experiments and under natural rainfall conditions. The small amount of flow at the trench occurred only under the highest rainfall intensities (above 15 mm h⁻¹), and was sporadic. The two wells located at the base of the plot did not detect any saturation during the experiment, showing that the percolation of the sprinkled water must have gone deeper before generating any consistent lateral flow downslope. Any downslope flow is therefore expected to be lower than their depth (2.00 and 2.40 m from the forest road surface).

The average value of VWC-based celerity in the deep WCR probes (707 ± 234 mm h⁻¹), point-based, was lower than the average value of celerity derived from MICS (971 ± 625 mm h⁻¹) (Table 4). Wetting front measurements were in close
agreement with one another, despite the different time steps of the celerity estimates, from 15 min for the TDR probes, to 105 min for the time-lapse ERT. This suggests that MICS methodology applied to time-lapse ERT provided a suitable estimate of flow movement through the soil profile under the conditions observed here.

MICS helped to identify the lower infiltration rate at the bottom of the plot (Figure 14). Corroborating this behaviour, the deeper WCR probe located at the bottom site in the plot consistently reacted with a longer lag time than the others, and therefore had a value of celerity only half that of the upper sites (Table 4). The reason for this could depend on changes in permeability, possibly linked to disruption during the construction of the forest road, causing a different pattern of infiltration in the lower plot. Moreover, the lower part of the plot received somewhat lower sprinkling intensities, in part due to a deliberate decision to avoid water falling on the roof of the trench.

MICS results showed no expansion in the downslope direction of the infiltration plume at the three time steps (Figure 14): the movement of water through the soil cannot be detected with MICS at depths further than 2-3m. Our results on in situ measurements (Section 3.4.2) showed that there is fine-scale variability in the soil structure, and that fine-scale preferential flow is not captured by the coarser resolution of the MICS methodology (Figure 14). MICS could not therefore be used to draw clear conclusions on lower boundaries for generation of lateral flow. This is partly due to the sensitivity of the ERT method, which is decreasing with depth. On the other hand, MICS requires a high resistivity contrast between the electrically conductive infiltration and the surrounding medium. Despite the very conductive salt tracer solution used (Section 3.4.5.1), the physical properties of the bedrock below 2.5 m depth, are responsible for a highly conductive pre-sprinkling signal (lower contrast with the surrounding medium), therefore disrupting the capability of MICS to detect infiltration pathways.

The highly permeable material, on which the soil is developing, (Section 3.2) is responsible for the strong prevalent vertical direction of flow through the subsurface. In turn, the subsurface topography is likely controlling lateral flow
generation. Although not observed, it is hypothesized that, below 200 cm depth, where the slate can still be infiltrated by water (as discussed by Juilleret et al., 2016), more consistent lateral flow takes place.

### 3.5.2 Combining celerity and velocity to detect preferential flow

Maximum velocities, estimated by initial tracer detection in suction lysimeter samples, were tracer-dependent and on average 109 ± 89 mm h\(^{-1}\) for Cl\(^-\), 178 ± 199 mm h\(^{-1}\) for Br\(^-\), and 604 ± 611 mm h\(^{-1}\) for Li\(^+\) (averaged from Figure 14). The observed high variability between maximum velocities of different tracers indicates a complex pattern of movement of tracers through the soil.

In Figure 7 we showed how the faster velocity can coincide with the wetting front but has an upper limit of the celerity (i.e. it can be equal to the celerity but not higher, unless detected earlier in lysimeters than in the moisture response, Section 3.3.3). At most of the measurement points and times, celerities were quicker than maximum velocities (Figure 14 and Figure 12). Only on March 13\(^{th}\) the maximum velocities (indicated by the tracer arrivals) were faster than the celerities (as indicated by changes in VWC) on average of 0.2% at 10 cm depth, and 2.6% at the deeper probes (but in location S2 celerities were still higher than velocities). For the other days, celerities were on average 2.7% higher than velocities at 10 cm depth and 6.4% at the deeper probes.

This “paradoxical” behaviour could be explained by intermittent and spatially localised preferential pathways as macropore flow, likely linked to roots, or channelled via horizontally layered stones. In this interpretation, preferential flow would need to deliver some solution to the suction lysimeters before the WCR probe located above them could detect wetting.

Even if differences between velocities and celerities may be intensified by the lower time resolution of the suction lysimeters sampling with respect to the WCR, and the depth at which celerities are measured (50-80 cm depth for WCR probes and 80-90 cm for suction lysimeters), there were other indications supporting a preferential flow type of process. The apparent porosity \(\varepsilon_a\) calculated from MICS at the three time steps following the tracer injection (Experiment 1) ranged between
1.4 and 12%. The average apparent increase in VWC in the wetted volume is therefore relatively small, particularly in the deeper WCR probes (Section 3.4.5.4). Given the rates of infiltration applied and the $\varepsilon_a$ values, this suggests fast and possibly preferential flow pathways.

Finally, a preferential type of flow is corroborated by trench flow characteristics. Trench flow main characteristics were: (i) intermittent flow during Experiment 2, even in presence of relatively constant rainfall; (ii) a very high variability in the concentration of tracers at the trench, with differences of more than 4 standard deviations between tracer concentrations of samples taken 5 min apart at same depth in the trench. Sporadic and spatially restricted outflow was also described by Kim et al. (2005), in a hillslope characterised by shallow soils formed in colluvium and glacial till. At our site, the highly variable concentrations of the intermittent flow to the trench had all lower concentrations than sprinkled concentrations.

Since trench concentrations are lower than the applied concentrations, this indicates that some displacement of stored water takes place even given fast preferential flow response. These direct flows to the trench, not subject to as much mixing as in the in the suction lysimeters (due to the difference in the sampling interval, lower for the suction lysimeters), are therefore not just a simple preferential flow of applied water, but a more complex flow dynamic. The imbricate structure of the coarse clasts, oriented parallel to the slope, could be driving the flow laterally (as proposed by Heller and Kleber, 2016, on periglacial cover beds), favouring a preferential flow network.

### 3.5.3 Tracer dynamics

Experiment 2 showed lower celerities than Experiment 1 (Figure 12), despite input intensities of a similar magnitude of Experiment 1, step 2 (Table 2). The lower values of celerities might be due to compaction of the soil around the probes over the period between the experiments, but could also be a consequence of change to the soil structure as a result of chemical processes following the addition of the tracer solution during Experiment 1 (Wendroth et al., 2011; Klaus et al., 2014).
Indeed, applying large amounts of salt to the soil surface can generate tracer-dependent changes in the soil structure (Perkins et al., 2011; Yalamanchali, 2012; Yousefi et al., 2014). High concentrations of cations, particularly $K^+$ and $Na^+$, are known to be responsible for a decrease in permeability and a reduced hydraulic conductivity (Rengasamy and Olsson, 1991). Due to the experiments, $Na^+$ had an average value of 174.00 ± 80.00 mg L$^{-1}$, and concentrations of $K^+$ were also raised to an average of 27.00 ± 10.00 mg L$^{-1}$.

Values of maximum velocities were very different across tracers, indicating strong dependence on the tracer used. Cl$^-$ maximum velocities were lower than both Br$^-$ and Li$^+$, while Li$^+$ had the highest maximum velocities (Figure 14).

Our interpretation depends on comparing celerity responses with conservative tracer responses. The non-uniformity of the rainfall intensity surely has an influence on the velocity/celerity relationship (Beven, 2012). Biogeochemical interactions and sorption are considered as the primary reasons for tracer different behaviour.

Understanding soil-tracer interactions is extremely difficult. In an effort to understand the differences in the velocities measured during the experiments, we briefly outline the processes that might affect tracer movement:

i. **Anion exclusion.** Cl$^-$ and particularly Br$^-$ can be transported through pores slightly faster than water molecules, due to the anion exclusion phenomenon, linked to the repulsion of anions from the negatively charged soil particles (Flury and Wai, 2003).

ii. **Chlorination.** The soil organic matter can instantaneously trap Cl$^-$ in the upper soil layer (which is enriched in organic matter) (Bastviken et al., 2007).

iii. **Anion retardation.** Salt addition affected the dominant charge of the soil. The strong content of $Na^+$ and $K^+$ could have given a positive charge to the soil, generating the conditions for anion retardation (due to sorption, see Sposito, 1989). In support of this hypothesis, salt aggregates had been observed on the soil surface (primarily NaCl and KCl).
Chlorination may have slowed down Cl\(^-\) respect to Br\(^-\), and some combination of factors may have accelerated the passage of Li\(^+\) explaining the higher maximum velocity values observed in Figure 14. After one year of natural rainfall, any residual effect of (i), (ii) and (iii) could have been mitigated, though we do not have direct evidence to support or refute this. We have no particular evidence that any of these processes might prevail over simple conservative transport, nor it was not the aim of this study to explore such chemical processes.

Additional information about mixing and tracer presence in the soil is provided by the multi-parameter sensor located in the middle of the plot (Figure 8). The salt sprinkled during Experiment 1 remained in the soil long after the experiment (Figure 8). The strong signal of EC in response to natural rainfall events shows remobilisation of the salt stored in the soil matrix, particularly during the heavy rainfall events in summer of 2014 (Figure 8.a). Soil analysis performed in autumn 2014 (i.e. 6 months after Experiment 1) strengthens this point: there were significant amounts of Cl\(^-\) and Br\(^-\) stored in the soil, to be remobilised during later rainfall events (Section 3.4.2). In the same way, Br\(^-\) was found in all the samples collected during Experiment 2, both at the trench and in the suction lysimeters (Section 3.4.2).

Chemical transport processes were present at the site well after the experiment. Remobilisation was peaking at the same time as the VWC peaks, therefore suggesting a system limited by transport. The salt was finally depleted towards the end of the summer, after a total of 500 mm of natural rainfall had infiltrated. Rainfall events following the summer period (additional 250 mm) did not cause the same release of tracers. The system was therefore limited by supply in this period (Figure 8.b), even though there was still residual tracer within the soil matrix suggested by the suction lysimeter samples (Section 3.4.2). In March 2015 a strong response was observed due to the last application of tracer (Figure 8.c).

### 3.6 CONCLUSIONS

The relationship between tracer velocities and wave or wetting front celerities is essential for understanding the complexity of flow from hillslopes to the stream. No experimental studies have yet connected estimates of the maximum velocity and
wetting front derived from state-of-the-art experimental techniques. To fill this gap, the maximum velocity and the celerity responses were explored in a plot located in the Weierbach catchment, where subsurface flows are known to contribute to riparian zone wetness and streamflows. Maximum tracer velocities and wetting front celerities were determined at plot scale using a three-fold monitoring protocol (including artificial tracers, time domain reflectrometry and time-lapse electrical resistivity tomography).

This study demonstrated the potential of different measurement approaches in facilitating the interpretation and quantification of infiltrating water flows. This work demonstrated that MICS, can help to understand wetting front dynamics, but it cannot capture local wetness patterns/lateral flow. The ERT method, as used here, does not detect wetting fronts or tracer transport at depths further than 2-3 m depending on the grouping criteria, due in part to the coarse resolution and in part to the characteristics of the bedrock (in particular its low porosity and resistivity).

It was found that tracer-specific properties influenced the response in terms of maximum velocity. In particular, Li^+, the last tracer used, reached the measurement points with velocities much higher than Br^−, and both were detected quicker than Cl^−, the first tracer to be employed and the more abundant in the input water (and the only one being naturally present in this soil). Moreover, tracers and soil compression during Experiment 1 potentially altered the soil structure and may have influenced the celerity estimates. A more extensive soil survey is being undertaken to understand tracer interactions at this soil.

No lateral flow was observed in the trench apart from a few preferential pathways.

Preferential flow processes were indicated by three different results: (i) maximum velocities apparently greater than celerities observed during experiment 2, (ii) scattered trench flow response with highly variable tracer concentrations and (iii) very low range of apparent porosity calculated using both MICS and deep VWC.

Maximum velocity information proved to be essential to understand flow dynamics in response to sprinkling, while information on the wetting front alone
would have missed important processes. This analysis demonstrates that measuring tracer velocities was of greater importance for understanding hillslope dynamics than capturing only celerity information. It also demonstrates the value of tracer data, soil moisture and ERT data at high time resolution, for interpreting hillslope dynamics. The results described in this study pose the basis for integrating in a simple way measures of celerity and maximum velocity into hydrological studies. The conditions required for the lateral connectivity to be present remain unknown and are the focus of further analysis.
4 HILLSLOPE RESPONSE TO SPRINKLING AND NATURAL RAINFALL USING VELOCITY AND CELERITY ESTIMATES IN A SLATE-BEDROCK CATCHMENT

ABSTRACT

Subsurface flow is recognized as a dominant mechanism in runoff generation. However, bedrock type and fracture orientation controls on flow direction, velocity and celerity remain poorly understood. Here we investigate the dominant controls on subsurface flow direction in a slate bedrock headwater catchment characterised by double peak discharge responses. We analyse the relative roles of surface slope and the bedrock cleavage in controlling flow pathways. For this purpose, we performed plot sprinkling experiments at a site located 40 m upslope from the stream channel using Br⁻ as a tracer. Tracer concentrations were then measured at a well downslope from the plot and at various locations along the stream. Velocities were estimated from tracer concentrations and celerities were estimated using well and stream hydrometric responses. Our results indicate that the single or first peak of double-peak events is rainfall-driven (controlled by rainfall) while the second peak is storage-driven (controlled by storage). The comparison between velocity and celerity estimates suggests a fast flowpath component connecting the hillslope to the stream, but velocity information was too scarce to support such a hypothesis. In addition, different estimates of celerities suggest a seasonal influence of both rainfall intensity rate and residual water storage on the celerity responses at the hillslope scale. At the catchment outlet, the total mass of Br⁻ measured in the stream was about 2.5% of the application. Further downstream, the measured mass of Br⁻ was about 4.0% of the application. This demonstrates that flowpaths do not appear to align with the slope gradient. In contrast, they appear to follow the strike of the bedrock cleavage. Our results have expanded our understanding of the importance of the subsurface, in particular the underlying bedrock systems, proving the importance of cleavage orientation in controlling subsurface flow direction. This work further demonstrated the importance of quantifying the extent of fractures as well as their orientation relative to dominant topographically related flowpaths.

Contribution: I was responsible for designing, implementing and executing the field experiment, collecting and analysing the data and writing.

4.1 INTRODUCTION

Subsurface flow can be a dominant mechanism in runoff generation and has been widely investigated (Whipkey, 1965; Hewlett and Hibbert, 1967; Dunne, 1978). Subsurface flow takes place both in the soil matrix, that over time may generate the dominant flux (Gilman and Newson, 1980; Jones and Crane, 1984; Uchida et al., 2005; Beven, 2010), and in soil cracks located between the soil and an impeding layer, earthworm burrows, root channels or other forms of macropores which enable the movement of water (Beven and Germann, 1982; Jackson, 1992; Bryan and Jones, 1997; Chappell, 2010).

Runoff generation processes are typically studied at the hillslope scale (Dunne, 1978). Notwithstanding recent advances in measuring techniques, measuring subsurface flow, as well as the subsurface properties that control subsurface flow, remains impracticable (Gabrielli et al., 2012; Wienhöfer and Zehe, 2014; Hale and McDonnell, 2016).

Besides the soil properties, the bedrock structure can have a strong influence on subsurface runoff. Although hard bedrock is often considered impermeable (Weyman, 1973; Tromp-van Meerveld et al., 2007; Wrede et al., 2015), this assumption is often “hopeful rather than realistic” (Beven, 2006c). Fractured bedrocks are very common in Europe (Lorz et al., 2011), and flow through bedrock can be substantial (Tromp-van Meerveld et al., 2007; Padilla et al., 2015). Hale et al. (2016) identified subsurface permeability structures as the main control on water storage and release.

Permeable bedrocks pose additional complexity regarding the identification of subsurface water release to the stream (Sklash and Farvolden, 1979; Cook et al., 2003). The geometry of fractures, which depends on the parent lithology and history (Onda et al., 2001; Chappell et al., 2007), can cause extreme spatial variability of hydraulic conductivity and groundwater flow rate (Cook et al., 1996, 2003). In order to understand how fractured bedrocks control hydrologic response it is necessary to describe each of the involved subsurface flowpaths and storage structures (Banks et al., 2009; Hale et al., 2016).
Differences between velocities and celerities are thought to explain the rapid runoff of stored water during rainfall events (McDonnell and Beven, 2014). However, few studies to date have quantified in-situ velocities and celerities. Novel model frameworks consider both celerity distributions, which manifest themselves in the hydrograph, and velocity distributions, manifested in tracer responses (Davies et al., 2011; Laine-Kaulio et al., 2014; Birkel and Soulsby, 2015; Soulsby et al., 2015; Scudeler et al., 2016). In a framework based on velocity/celerity analysis, the hydrograph and flow path velocity characteristics are integrated. While average celerity and average velocity can be estimated at catchment scales (Rasmussen et al., 2000), there have been very few studies that have attempted to study the characteristics of both celerities and velocities at field scale (Scaini et al., 2017a).

Subsurface flow pore water velocities can be inferred using geochemical tracers (Harr, 1977; Sidle et al., 1995). Tracer studies are employed to understand how quickly, in what concentration and from what sources does water reach the stream. Tracer input-output relationships are used to estimate the transit-time distributions of water in the catchment (Nyberg et al., 1999; McGuire et al., 2007; Klaus et al., 2015) and can be useful to characterise flowpaths (Trudgill et al., 1983; Wienhöfer and Zehe, 2014). Unfortunately, the interpretation of the tracer results is often biased by the spatial and temporal resolution and analytical protocols of tracer collection (Weihermüller et al., 2007; Abbott et al., 2016).

Our work is undertaken in the Weierbach experimental catchment in Luxembourg, a site underlain by Devonian slate (Juilleret et al., 2011; Moragues-Quiroga et al., 2016) characterised by double-peak runoff responses (Martínez-Carreras et al., 2016). We build on previous work based on estimates of maximum velocities and flow celerities which showed that, at the plot scale, the flow direction in the soil is predominantly vertical, until the relatively impermeable boundary of the bedrock system is encountered, which is located below 2-3 m depth (Scaini et al., 2017a). The conditions required for the onset of lateral subsurface flow had not been previously identified and are the focus of this work.
Our objective is to quantify celerities and velocities in the path between the hillslope and the stream, by analysing plot-scale artificial sprinkling experiments and stream chemistry. Specific research questions include:

(i) How are groundwater and streamflow dynamics related to rainfall inputs?

(ii) How do bedrock structural properties, particularly cleavage orientation, influence tracer transport from plot to stream?

(iii) How does tracer transport relate to estimates of celerities?

The manuscript is structured as follows: Section 2 presents the research site, followed by Section 3 where the equipment used is presented, and Section 4, describing the sprinkling experiments and the analysis applied. Section 5 describes results on hydrometric response to rainfall and sprinkling, tracer detection, and velocity and celerity estimates. Section 6 addresses each of the research questions providing individual discussion points. The paper concludes summarizing the key findings of the study in relation to each of the research questions.

4.2 DESCRIPTION OF THE EXPERIMENTAL FIELD SITE

The Weierbach, an experimental site located in the North-West of Luxembourg, is a forested catchment underlain by Devonian slate. Altitudes range from 465 to 512 m a.s.l. Average annual rainfall is 812 mm/a (2007-2016) and annual runoff ratios are around 0.55 (2005 to 2008) (Martínez-Carreras et al., 2016).

Geologically, the catchment presents Pleistocene Periglacial Slope Deposits where a soil develops covering the in situ compact and slightly weathered slate bedrock also called Saprock (Eggleton, 2001; Juilleret et al., 2011; Martínez-Carreras et al., 2016). The whole regolith classification is Dystric Cambisol (Ruptic, Endoskeletic, Siltic, Protospodic) according to the WRB reference (WRB, 2015) overlying a Regolithic Saprock (Vertifractic, Rootic) [Slatic] (Juilleret et al., 2016). The 64 m² plot used for the sprinkling experiments is located 40 m uphill from the stream, on the left bank (Figure 15). The slope is steep (average of 10°) and perpendicular to the stream.
Rock cleavage or foliation is a property of rocks, referring to layering along approximately parallel surfaces (Singhal and Gupta, 2010). The cleavage plans lead to preferential cracks within the rock. Depending on extent connectedness and orientation, cracks can have a variable impact on water movement. At the hillslope site, a geological compass and clinometer measurement of the strike and dip of the cleavage plans showed on average 70 N degrees and a vertical dipping, in other words diagonally respect to the surface slope (a sketch of its orientation is shown in Figure 15.b).

Figure 15. (a) Location of the Weierbach catchment, in Luxembourg. The enlarged red box shows the location of the chosen hillslope within the Weierbach catchment. (b) The box shows the plot used for the sprinkling experiments, the location of the well GW3 (indicated by a blue square), and the stream gauge, SW (indicated by a grey triangle). (c) Sketch of the hillslope with the automatic (stars) and manual (circles) sampling points used during Experiment 2 to monitor the chemical composition of the stream water response to sprinkling. The location of the 2 wells GW1 and GW2 are also shown.
Previous work assumed that significant lateral (parallel to the surface topography) subsurface flow would occur in the fractured bedrock (or Saprock) or in the stony basal layer of the periglacial cover beds (Wrede et al., 2015; Juilleret et al., 2016). Our previous analysis showed that the relevance of shallow lateral flow at the site is very low (Scaini et al., 2017a). Thus subsurface hillslope contributions to streamflow should are expected only below 2-3 m in the slate bedrock. This zone, however, is characterised by low porosity and resistivity, which complicates the detection of lateral flow using geophysical methods. Here we attempt to examine the hillslope to channel flow pathways by characterising the release of water from the hillslope, monitoring the outflow to the stream using tracers.

4.3 MATERIALS

Considering the hillslope as a system, we present the equipment used to generate or measure (i) input of water and tracers; (ii) internal states, including water content and concentrations; (iii) output of water and tracers in the stream.

4.3.1 Input

Natural precipitation was recorded by a tipping bucket rain gauge (Campbell Scientific Ltd., model 52203) located 3.5 Km from the experimental catchment, at the Roodt automatic weather station. The high density of vegetation hindered measurements of natural precipitation closer to the experimental plot.

4.3.2 Internal states

In order to detect lateral flow beneath the collection troughs, two 2-in diameter groundwater wells were installed at the base of the plot. Drilling was performed from the surface of the forest road, on the two sides of the roof covering the base of the plot. The two wells were drilled to 2 (GW1) and 2.4 m (GW2) depth and equipped with pressure sensors (OTT CTD), to monitor water table depth and temperature (Figure 15.c). Additionally, a 3-in diameter groundwater well (GW3), located 12 m from the stream (Figure 15.b), was monitored for water table depth fluctuations, electric conductivity (EC) and temperature (using another OTT CTD sensor). The well GW3 was drilled in 2009 and was sited to follow the cleavage strike (Figure 15.b). The chemical composition of the well water was analysed with grab samples collected at
variable time steps during the experiments. To characterise the evolution of the concentrations of the well outside the artificial experiments, bi-weekly samples were taken during a period of 2 years.

Finally, a 2-in groundwater well located on the plateau uphill of the study plot (GW4) was monitored for water table depth fluctuations, electric conductivity (EC) and temperature starting from September 2014 using a multi-probe TD-Diver (Schlumberger Water Services). As the monitoring was not permanent during the studied period, this well was used mostly as a reference for overall water table fluctuations.

4.3.3 Outputs

Stream water level at the outlet (SW) was measured using a pressure transducer (ISCO 4120 Flow Logger) in combination with a V-notch weir. EC at the outlet was also continuously monitored using a conductivity probe (WTW 3310). The chemical composition of the stream water at SW was monitored during a period of 2 years using manual bi-weekly samples. Additionally, a high resolution stream sampling set-up was undertaken during the sprinkling experiments. The stream was sampled at 3 different locations: (i) at SW (the outlet) (ii) 30 m upstream (upstream respect to the study hillslope) and (iii) 15 m downstream using automatic water samplers (ISCO 6712, Figure 15.c). Manual samples were also manually collected at 2 intermediate locations (Figure 15.c).

4.4 METHODS

This section describes the measurements performed during the sprinkling experiments (4.4.1) and the analyses of the measured data collected during the experiments (4.4.2).

4.4.1 Sprinkling experiments

Artificial irrigation experiments were carried out between March 31st and April 10th 2014 (Experiment 1) with the aim to explore plot-scale generation of shallow lateral flow. Experiment 1 raised the need for additional monitoring of the stream.
Experiment 2 was therefore performed using different tracers between March 11th and 16th 2015. For a full description of the experiments, see (Scaini et al., 2017a).

**4.4.1.1 Plot scale monitoring: Experiment 1**

During Experiment 1, solutions containing different concentrations of NaCl and KBr were used to sprinkle the area. The sampling protocol was mostly carried out at the plot scale to characterise plot response. Given some shortcomings in the experimental design (absence of shallow lateral flow, limited information on deeper storage, need of including stream sampling to study the release of water from the hillslope, described in Scaini et al., 2016) we refined the methodology and experimental design in a second experiment.

**4.4.1.2 Stream intensive sampling: Experiment 2**

During Experiment 2, solutions of water and NaCl were applied, and additional data were used to monitor hillslope response. The stream was sampled at high frequency at 3 locations (Figure 15.c, stars) using ISCOs programmed at 30 minutes time step during the experiment, and progressively longer time steps for a period of 3 weeks after the experiment (from 1h to 6h time step). Manual samples were taken at 2 locations at hourly time step during the experiment (Figure 15.c, circles).

**4.4.2 Analyses of measured data**

**4.4.2.1 Hydrometric monitoring**

During the experiments, the water table depth fluctuations, EC and temperature were recorded at 15-min intervals in GW3. In order to capture lower lateral flow, the two wells at the bottom of the plot, GW1 and GW2 in Figure 15.c, recorded water table height, temperature and EC at variable time step (up to 5 seconds time step during the experiments). Runoff and EC at the outlet (grey star, Figure 15.b) were continuously recorded at 15-min intervals.

**4.4.2.2 Natural rainfall events analysis**

A series of natural rainfall events were considered for the analysis. The selection criteria focused on rainfall events of a total of at least 15 mm, to analyse event
magnitudes as much as possible similar to the sprinkling. Each event was considered separately when the time elapsed from the previous event was at least 3 h, as during the sprinkling experiments each day’s irrigation was carried out non-stop or stopped for a period between 1 and 3 h. Rainfall intensity, catchment wetness (in terms of Antecedent Precipitation Index, API, calculated for 30 and 7 days prior to the rainfall event), and the timing of stream and groundwater response were calculated for each rainfall event. Cross-correlation was used to calculate the lag time for which the correlation between rainfall and stream discharge was maximum. In the same way, the lag time corresponding to the maximum correlation between rainfall and water table depth was also computed (in this case, maximum inverse correlation).

Double peaks in the hydrograph were observed from late autumn to early spring when soil moisture values are higher. There were also a few cases where summer double peak events occurred linked to large precipitation events (Martínez-Carreras et al., 2016). Cross-correlation was also computed for the double peak events, by calculating both the lag time for which the correlation between rainfall and stream discharge was maximum, and the lag time for which inverse correlation between rainfall and water table depth was maximum. The results of cross-correlations were used to check for differences between single and double peak discharge and groundwater response timings, by comparing the lag times corresponding to maximum cross-correlation of the single and double-peak events as well as their corresponding correlation coefficient.

4.4.2.3 Tracer monitoring

The arrival time of the tracers to each sampling point was determined by comparison with the background values. Tracers dissolved in the input water were used to track the water knowing precisely its input times and chemical composition.

All collected water samples were filtered using Acrodisc syringe 0.45 µm filters (Pall Corporation) in order to be analysed for chloride (Cl⁻) and bromide (Br⁻) concentrations using ionic chromatography (Dionex ICS-5000). The detection limit of the analyses was 0.01 mg L⁻¹ for Cl⁻ and 0.02 to 0.01 mg L⁻¹ for Br⁻.
Background anions and cations in the stream and groundwater were measured over a three year long bi-weekly sampling campaign, between 2011 and 2013. The average value of the background Cl\(^-\) concentration in the input water was 3.33 ±2.45 mg L\(^{-1}\). No detectable Br\(^-\) concentrations were found in the background samples. The average EC value in the stream water was 45 ±10 µS cm\(^{-1}\). Cl\(^-\) detected in the well over the 3-years bi-weekly campaign were equal to 5.15 ±0.42 mg L\(^{-1}\), while EC had mean value of 107 ±6 µS cm\(^{-1}\). A linear regression model to estimate Cl\(^-\) from EC was fitted to such data (Chang et al., 1983; Siosemarde et al., 2010).

Br\(^-\) concentrations during the high frequency sampling stream campaign (Experiment 2, Section 4.4.1) were used to calculate the mass of Br\(^-\) leaving the system. This was performed by (i) interpolating the missing concentration data to hourly time-step; (ii) multiplying Br\(^-\) concentrations to discharge (available at hourly time step) to obtain the load; (iii) summing up all the values to obtain the total mass of Br\(^-\).

### 4.4.2.4 Velocity estimates

Given the importance of both celerity and velocity in storage-discharge responses (McDonnell and Beven, 2014), estimates of both quantities were derived using a data-based approach. For both velocities and celerities, a time difference and distance are required.

A velocity distribution summarizes the range of velocities water is travelling through all the various flow pathways in the subsurface. Wider distributions are indicative of larger heterogeneities and variability of flow pathways, whereas narrower distributions are representative of more homogeneous conditions (Davies and Beven, 2012). Maximum velocity can be derived as the first detection of a tracer at a measurement point and represents the fastest flow pathway (McDonnell and Beven, 2014). Mean velocity provides information on propagation, storage and remobilisation of tracers.

Each type of velocity and the information of length and time used to compute each velocity are shown in Table 5.a. The arrival times of Br\(^-\) and EC (used as a proxy for salt tracer) to well and stream, were used to estimate information on velocities.
For the time information, each velocity was computed using tracer application as a starting point.

At the well GW3, the maximum velocity was computed by dividing the distance between the plot and the well by the time at which a start of EC rise (corresponding to the time at which the tracer plume reached the well) occurred ($v_{\text{max},w}$) (Table 5.a). The well EC peak provided time information regarding the arrival of the maximum concentration of the plume, an approximation of the mean velocity, $\bar{v}_w$. In the same way, the plot-stream downslope distance was divided by the time between start of tracer application and start of the EC rise in the stream, to compute the maximum velocity ($v_{\text{max},s}$). The plot-stream downslope distance was divided by the timing of the stream EC peak to estimate the mean velocity, $\bar{v}_s$.

Table 5. Definition table for velocities and celerities used throughout the paper. The definitions make reference to Figure 2.

<table>
<thead>
<tr>
<th>a) symbol</th>
<th>Type</th>
<th>length</th>
<th>time (from tracer injection)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{\text{max,ws}}$</td>
<td>maximum velocity</td>
<td>from GW3 to stream</td>
<td>start EC rise in SW</td>
</tr>
<tr>
<td>$\bar{v}_{ws}$</td>
<td>mean velocity</td>
<td>from GW3 to stream</td>
<td>peak EC in SW</td>
</tr>
<tr>
<td>$V_{\text{max,w}}$</td>
<td>maximum velocity</td>
<td>from plot to GW3</td>
<td>start EC rise in GW3</td>
</tr>
<tr>
<td>$\bar{v}_{w}$</td>
<td>mean velocity</td>
<td>from plot to GW3</td>
<td>peak EC in GW3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>b) symbol</th>
<th>Type</th>
<th>length</th>
<th>time (from rainfall start)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{su}$</td>
<td>Initial event celerity</td>
<td>average riparian zone length</td>
<td>start discharge rise</td>
</tr>
<tr>
<td>$C_{ss}$</td>
<td>Integral event hydrograph celerity</td>
<td>average hillslope length (including divide in second peaks)</td>
<td>peak discharge</td>
</tr>
<tr>
<td>$C_{wu}$</td>
<td>Initial hillslope celerity</td>
<td>Planar distance between well located on top (GW4) and on bottom (GW3) of the slope</td>
<td>start water table rise in GW3</td>
</tr>
<tr>
<td>$C_{ws}$</td>
<td>Integral hillslope celerity</td>
<td>Planar distance between well located on top and on bottom of the slope</td>
<td>water table peak in GW3</td>
</tr>
</tbody>
</table>

4.4.2.5 Celerity estimates

Celerity is defined with respect to the speed with which a perturbation to the flow propagates through the flow domain (McDonnell and Beven, 2014). Celerity responses depend on the nature of the perturbation and the antecedent wetness,
which in our case is determined by the artificial and natural rainfall events. Defining a consistent framework to calculate the spatial propagation of a perturbation is critical to be able to look at the celerity estimates.

For the purposes of analysis we need to provide working definitions of celerities that can be calculated from the data. For the water table, we can assume that the first response following rainfall will be a good indication of first wetting celerity in the unsaturated zone (classically as a wetting front shock, Beven, 1981), but here more likely as a result of preferential flow. In the case of the stream, the initial rise will be a combination of the initial response in the riparian area and routing through the channel network. We can also define celerities based on the time to peak of the water table and hydrograph. For the water table response, this will represent an average for the unsaturated zone and saturated zone response upstream of the well. For the discharge, it represents and integral of the hillslope and channel network responses, including likely fast pathways through the bedrock fractures of hillslopes, as recent research suggested (Wrede et al., 2015; Jackisch et al., 2016; Martínez-Carreras et al., 2016). Thus we calculate the following celerity indices, as described in Figure 16 and Table 5.b, using the natural rainfall events described in Section 4.4.2.2:

1. Initial event celerity, $C_{su}$, was estimated using the time frame between rainfall start and start of discharge rise at outlet;

2. Integral event hydrograph celerity ($C_{ss}$) was estimated, using the time frame between rainfall start and peak discharge at the outlet;

3. Initial hillslope celerity ($C_{wu}$) was estimated using the time frame between rainfall and start of water table response in GW3;

4. Integral hillslope celerity ($C_{ws}$) was estimated using the time frame between rainfall start and peak of water table response in GW3.

To define the relevant downslope distances, we used a 5x5 DEM. In the single or first peak events, the distance was defined as the mean downslope distance between the stream and the hillslope (slope >6.5°). In the double-peak events, the mean downslope distance between the stream and the divide (slope <6.5°) was used to include the plateau, as in the formulation of Martínez-Carreras et al. (2016) ($C_{ss}$, ...
Figure 16. Definition sketch for celerity calculations. (a) The figure shows time series of rainfall, SW discharge and GW depth for an event in 2015 (Event 19, Table 2). Celerity measurements refer to the lag time from the start of rainfall to the start of water table response, here shown as GW3 depth (C_wu), start of discharge response (C_su), maximum value of GW3 depth (C_ws) and discharge peak (C_ss). (b) Spatial framework for the estimation of celerities and velocities. The symbols correspond to Table 1.
In the case of the well response, the fixed planar distance between the 2 wells located respectively on the plateau (GW4) and at the bottom of the slope (GW3) was used to compute information of celerity (Figure 16.b). Such measure was divided by the start of water table rise (to compute $C_{wu}$) and time of peak (to compute $C_{ws}$), both calculated from the start of the rainfall event.

4.5 RESULTS

4.5.1 Response to natural rainfall and to sprinkling

Table 6 summarizes the characteristics of 21 natural events (12 in 2014 and 9 in 2015) having cumulative rainfall higher than 15 mm (Section 4.4.2.2). In addition to the characteristics of each rainfall event, the maximum cross-correlations between rainfall and groundwater, and rainfall and discharge responses are given for each event. GW1 and GW2, were dry throughout the observation period, and were therefore not included in the analysis.

The relationship between time series was analysed as a first check for relationships between variables. The average of the maximum correlation coefficients ($R$) between rainfall and discharge, as used to indicate the average lag time, was equal to 0.66. In all cases the corresponding lag time was below 1 h, showing a relatively homogeneous response of the discharge to rainfall in terms of timing (Table 6). In the case of Event 19, the maximum correlation occurred for the non-lagged discharge, showing that the response to rainfall was quicker than 15 minutes, one time step (Table 6). The maximum lag time between rainfall and water table response ranged between 0.5 and 12.5 h (Table 6), with maximum $R$ between 0.10 and 0.70, showing a more complex timing response. In all the single peak cases, the start of the discharge rising limb and discharge peak always preceded the first rise of the water table. In the cases where a double peak occurred, the discharge peak followed the maximum rise of the water table (measured from GW3), with peaks lagged between 1 and 3 h.
Table 6. Rainfall events with cumulative rainfall >15 mm and characteristics of the rainfall event: Event number, date, total mm, duration in hours, maximum intensity in mm/15min, maximum intensity in mm h⁻¹, API30 and API7. For each event, the maximum cross-correlation expressed in minutes of lag between rainfall and GW3 response and rainfall and SW discharge response are shown. **Bold**: double peak events. Coloured: events highlighted in Figure 3. Brackets: maximum correlation occurred for first peak only. X: absence of correlation.

<table>
<thead>
<tr>
<th>n</th>
<th>Date</th>
<th>mm tot</th>
<th>duration rainfall (h)</th>
<th>max mm/15min</th>
<th>max mm/h</th>
<th>API30 mm</th>
<th>API7 mm</th>
<th>GW3 lag min</th>
<th>SW lag min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>06/01/2014-07/01/2014</td>
<td>20.2</td>
<td>7.5</td>
<td>1.6</td>
<td>3.8</td>
<td>89.4</td>
<td>19.6</td>
<td>60</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>04/06/2014</td>
<td>18.9</td>
<td>13</td>
<td>3.3</td>
<td>5.0</td>
<td>62.9</td>
<td>0.1</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>11/06/2014</td>
<td>17.3</td>
<td>1.5</td>
<td>10.9</td>
<td>15.7</td>
<td>43.4</td>
<td>19</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>06/07/2014</td>
<td>16.2</td>
<td>3.5</td>
<td>5.4</td>
<td>9.9</td>
<td>47.6</td>
<td>12.6</td>
<td>180</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>08/07/2014</td>
<td>16</td>
<td>15</td>
<td>1.2</td>
<td>4.0</td>
<td>64.1</td>
<td>22.2</td>
<td>192</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>09/07/2014</td>
<td>21.7</td>
<td>12</td>
<td>1.4</td>
<td>4.1</td>
<td>80.1</td>
<td>38.2</td>
<td>240</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td>24/07/2014</td>
<td>18.5</td>
<td>0.5</td>
<td>9.7</td>
<td>18.4</td>
<td>101.6</td>
<td>0.7</td>
<td>45</td>
<td>15</td>
</tr>
<tr>
<td>8</td>
<td>29/07/2014</td>
<td>17</td>
<td>1.75</td>
<td>7.1</td>
<td>8.3</td>
<td>108.3</td>
<td>24.4</td>
<td>90</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>08/08/2014-09/08/2014</td>
<td>23.7</td>
<td>5.25</td>
<td>6.1</td>
<td>8.6</td>
<td>109.8</td>
<td>22.9</td>
<td>270</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>10/08/2014</td>
<td>22.8</td>
<td>7.5</td>
<td>12.3</td>
<td>12.7</td>
<td>114.9</td>
<td>49.7</td>
<td>330</td>
<td>15</td>
</tr>
<tr>
<td>11</td>
<td>11/12/2014</td>
<td>15.5</td>
<td>18</td>
<td>1.6</td>
<td>3.4</td>
<td>28.9</td>
<td>7.3</td>
<td>585</td>
<td>(15)</td>
</tr>
<tr>
<td>12</td>
<td>12/12/2014-13/12/2014</td>
<td>31.2</td>
<td>22.75</td>
<td>0.6</td>
<td>1.7</td>
<td>57</td>
<td>36.4</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>13</td>
<td>08/01/2015</td>
<td>31.7</td>
<td>21</td>
<td>1.2</td>
<td>6.0</td>
<td>84</td>
<td>5.3</td>
<td>(30)</td>
<td>(60)</td>
</tr>
<tr>
<td>14</td>
<td>15/01/2015</td>
<td>26.5</td>
<td>26</td>
<td>0.9</td>
<td>2.8</td>
<td>87.4</td>
<td>56.5</td>
<td>1920</td>
<td>1260</td>
</tr>
<tr>
<td>15</td>
<td>14/02/2015</td>
<td>19.8</td>
<td>20.5</td>
<td>3.6</td>
<td>6.6</td>
<td>71.6</td>
<td>23.3</td>
<td>75</td>
<td>15</td>
</tr>
<tr>
<td>16</td>
<td>29/03/2015-30/03/2015</td>
<td>20.9</td>
<td>26.5</td>
<td>2.1</td>
<td>4.6</td>
<td>27.2</td>
<td>8.6</td>
<td>135</td>
<td>30</td>
</tr>
<tr>
<td>17</td>
<td>04/08/2015</td>
<td>18.7</td>
<td>7</td>
<td>10.6</td>
<td>14.0</td>
<td>35.5</td>
<td>0.6</td>
<td>750</td>
<td>60</td>
</tr>
<tr>
<td>18</td>
<td>27/08/2015-28/08/2015</td>
<td>21.7</td>
<td>24</td>
<td>1.1</td>
<td>2.9</td>
<td>50.4</td>
<td>7.7</td>
<td>705</td>
<td>45</td>
</tr>
<tr>
<td>19</td>
<td>01/09/2015</td>
<td>32.3</td>
<td>8.25</td>
<td>2.4</td>
<td>8.8</td>
<td>71.5</td>
<td>25.2</td>
<td>180</td>
<td>&lt;15*</td>
</tr>
<tr>
<td>20</td>
<td>15/09/2015-16/09/2015</td>
<td>47.5</td>
<td>17.5</td>
<td>11.3</td>
<td>14.7</td>
<td>82.4</td>
<td>17.6</td>
<td>120</td>
<td>15</td>
</tr>
<tr>
<td>21</td>
<td>19/11/2015-20/11/2015</td>
<td>29.6</td>
<td>36</td>
<td>0.5</td>
<td>4.3</td>
<td>38.5</td>
<td>36.8</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

*The maximum correlation occurred for the non-lagged discharge.

Figure 17 shows the discharge-storage relationship (Figure 17.a) as well as the EC-well relationship (Figure 17.b), with a few events of more than 15 mm rainfall highlighted by colours (events 1, 2, 3, 7, 10, 12, Table 6). The event of December 2014, highlighted in yellow in Figure 17, generated the highest water table (reaching 1 m below soil surface) and discharge peak (up to 80 L s⁻¹). The relationship between water table depth and EC does not follow a clear pattern, even though we can see
the peaks due to the tracing experiments, where despite the absence of response in the water table, the EC rose to the maximum values for the series (Figure 17.b).

Figure 17. (a) Scatterplot showing the relationship between SW discharge and depth to water table in GW3. (b) Scatterplot showing the relationship between depth to water table and corresponding value of EC, both measured in GW3. In both graphs the full series of 2014 and 2015 are shown in grey, while few events are indicated by colours (events 1, 2, 3, 7, 10, 12, see Table 6).
The stream and GW3 were not affected by the experiments: both stream discharge and groundwater depth did not have a significant response during both Experiment 1 and Experiment 2.

Table 7 shows, for both Experiment 1 and 2, the minimum and maximum values of groundwater EC and depth to water table measured at GW3, and stream EC and discharge measured at SW. The maximum values of EC during the period following Experiment 1, resulting from the salt dissolved in the sprinkling water are given in brackets. Both experiments were conducted in low flow periods (discharge range 1-2 L s\(^{-1}\) in Experiment 1 and 4-7 L s\(^{-1}\) in Experiment 2).

Table 7. The minimum and maximum values of sprinkled rainfall, EC and water table depth (measured in GW3), EC and discharge (measured at SW) are shown. The maximum EC values occurred after the first experiment - likely due to arrival of sprinkled salts - are shown in brackets.

<table>
<thead>
<tr>
<th></th>
<th>Rainfall mm h(^{-1})</th>
<th>GW3 EC uS cm(^{-1})</th>
<th>GW3 depth m</th>
<th>SW EC uS cm(^{-1})</th>
<th>SW discharge L s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp 1</td>
<td>Max</td>
<td>23.4</td>
<td>136 (201)</td>
<td>1.96</td>
<td>73 (145)</td>
</tr>
<tr>
<td></td>
<td>Min</td>
<td>5.1</td>
<td>117</td>
<td>1.93</td>
<td>43</td>
</tr>
<tr>
<td>Exp 2</td>
<td>Max</td>
<td>28.4</td>
<td>176</td>
<td>1.89</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>Min</td>
<td>5.1</td>
<td>136</td>
<td>1.73</td>
<td>44</td>
</tr>
</tbody>
</table>

Figure 18 shows the time series of natural and sprinkled rainfall (a), GW3 depth to the surface and SW discharge (b), EC in SW (left y axis) and GW3 (right y axis) (c). Figure 18.d and 18.e show respectively stream and GW3 Cl\(^-\) and Br\(^-\) concentrations, expressed as mg L\(^{-1}\).

Following Experiment 1, detectable EC rises in GW3 were observed (Figure 18.c). Three distinct EC peaks were observed: (i) following Experiment 1; (ii) following Experiment 2; (iii) in late 2015 (indicated in Figure 18.c). The EC in GW3 started to rise on April 09\(^{th}\) and peaked on April 18\(^{th}\), 2014 with 201 µS cm\(^{-1}\). The closest sample analysed was taken on the April 19\(^{th}\), where EC was 179 µS cm\(^{-1}\) and Cl\(^-\) was 28.79 mg l\(^{-1}\) (Figure 18.d). The average value of the EC in GW3 rose from 107 ±6 µS cm\(^{-1}\) before Experiment 1 to 148 ±19 µS cm\(^{-1}\) after Experiment 1 (Figure 18.c). The second EC peak, following Experiment 2, was lower than the previous year, with a peak value of 176 µS cm\(^{-1}\) reached on March 14\(^{th}\) 2015. The third rise occurred in late 2015, slowly
rising starting in September 21st until its recession in November 11th, with a peak of 207 µS cm⁻¹ on October 23rd during a dry period (API7=3.5 mm; API30=30mm).

Figure 18. (a) Time series of hourly natural (black) and sprinkled (light-blue) rainfall. (b) GW3 depth to the surface (light blue) and SW discharge at outlet (red). (c) Stream EC (red) and GW3 EC (light blue), both expressed as µS cm⁻¹. (d) Cl⁻ (blue, left y axis) and Br⁻ (green, right y axis) concentration measured at SW. (e) Cl⁻ and Br⁻ concentration in GW3. Br⁻ concentrations below detection limit are not shown. Br⁻ concentrations in SW are ten times lower than GW3 concentrations.
In the stream, EC rose twice on the last 2 days of Experiment 1, April 09\textsuperscript{th} and 10\textsuperscript{th} 2014. Cl\textsuperscript{−} and Br\textsuperscript{−} were applied respectively to each of these events (Section 4.4.1.1). Stream EC started to peak around 13h30 on April 09\textsuperscript{th}, 6 h after the well EC started rising. The two stream EC peaks were sharp (both had duration of 4 h between start and fall), and occurred on the only 2 days where shallow lateral flow occurred, respectively 4h30 and 3h30 after the shallow lateral flow had initiated (Scaini et al., 2017a). The 2 peaks of stream EC were equal to 74.5 and 72.9 µS cm\textsuperscript{−1} respectively. The estimated amount of each peak’s Cl\textsuperscript{−} concentration was respectively 4.09 and 4.02 mg L\textsuperscript{−1} (using the calibration curve between EC and Cl\textsuperscript{−} described in Section 4.4.1.3).

The first few natural rainfall events after Experiment 1 did not generate any EC change in the stream (Figure 18.c). In July, between the 11\textsuperscript{th} and the 21\textsuperscript{st} an EC peak was detected at the stream outlet (Figure 18.c). The July peak reached the maximum of stream EC in the whole time series, reaching 145 µS cm\textsuperscript{−1}. The delayed peak in stream EC followed three important summer events: July 6\textsuperscript{th} (16 mm), 8\textsuperscript{th} (16.2 mm) and 9\textsuperscript{th} (21.6 mm), for a total of 53.7 mm in three days (API30 = 48.0 mm; API7= 9.4 mm). To understand this behaviour, we analyse the events of a similar magnitude (or higher) during the 2 year period comprising the events.

**4.5.2 Tracer detection**

In GW3, Cl\textsuperscript{−} detection rose from an average value of 5.15 ±0.42 mg L\textsuperscript{−1} before Experiment 1 to an average value of 7.88 ±6.64 mg L\textsuperscript{−1} after it (Figure 18.e). This suggests that significant amounts of Cl\textsuperscript{−} moved through the hillslope and likely reached the stream. The natural presence of Cl\textsuperscript{−} in stream water does not allow the data to be analysed unambiguously, as the average concentrations before (3.15 ±0.13 mg L\textsuperscript{−1}) and after (3.22 ±0.51 mg L\textsuperscript{−1}) the experiments were very similar. Therefore, we focus on Br\textsuperscript{−} as it was the only tracer that could be used to characterise hillslope response.

Figure 19 shows cumulative rainfall plotted against cumulative discharge in both 2014 and 2015. In light blue, highlighted by circles, Experiments 1 and 2 are shown. The time where Br\textsuperscript{−} was detected in GW3 and in SW are highlighted. Br\textsuperscript{−} was detected
on multiple samples in summer 2015: first, it reached SW in detectable quantities during the higher frequency sampling of Experiment 2 (Figure 18.e). Then, it was detected on multiple occasions between May 11th and 13th, June 24th and July 08th, and until September 08th 2015, with rising concentrations. During both summers, the stream was intermittently dry.

Figure 19. Cumulative rainfall/cumulative discharge indicating the presence of Br⁻ in SW (yellow) and GW3 (grey). Light-blue circles show the 2 experiments. A light-blue dashed line indicates the separation between 2014 and 2015.

With Experiment 1, a total of 5 Kg of KBr were released during sprinkling. Through the following months, Br⁻ was first detected in GW3 starting on June 11th, and was detected in 3 consecutive samples, until beginning of August 2014. Starting from August 20th, Br⁻ was not detected anymore in the well until Experiment 2, when Br⁻ was again detected in all samples between March 12th and March 23rd (Figure 18.e). Br⁻ concentrations in GW3 in this time period were on average 0.30 ± 0.25 mg L⁻¹.
In the stream, Br\textsuperscript{-} was detected only few months later, on August 06\textsuperscript{th}, 2014. Br\textsuperscript{-} detection in SW was limited to only 1 sample in 2014, with 0.04 mg L\textsuperscript{-1} (the one collected on August 06\textsuperscript{th}). In 2015 Br\textsuperscript{-} was detected again in the stream, in concentrations of 0.04 ±0.02 mg L\textsuperscript{-1} (Figure 18.d).

Figure 20 shows the relationship between GW3 and SW Cl\textsuperscript{-} (a), SW Cl\textsuperscript{-} and SW discharge (b), GW3 Cl\textsuperscript{-} and groundwater depth (c), GW3 Cl\textsuperscript{-} and GW3 EC (d). The same relationships are shown for Br\textsuperscript{-} in the right column (Figure 20.e, f, g, h). The scatterplots show that Br\textsuperscript{-} concentrations in SW are ten times lower than in GW3. Br\textsuperscript{-} was not detected in most of the samples (in SW, only 8 out of the 56 samples following tracer input, Figure 20.f). All the detections corresponded to low water table depth (Figure 20.g) and low flow days (below 5 L s\textsuperscript{-1}), apart from two cases with respectively 8.6 L s\textsuperscript{-1}, on 01/04/2015, and 20.6 L s\textsuperscript{-1}, 03/12/2015 (Figure 20.f). Moreover, Br\textsuperscript{-} concentrations were detected in SW mostly when the sample occurred on a non-rainy day (Figure 17). An exception is the last part of 2015, with 2 samples where Br\textsuperscript{-} was detected on rainfall events lower than 1 mm.

Experiment 2 stream sampling showed that there was significant Br\textsuperscript{-} remobilisation in later events. We observed similar or lower concentrations in the sampling points downstream with respect to 3 other sampling sites located upstream and on the topographical slope (Figure 15.c). At SW, the total of Br\textsuperscript{-} exported during the 1-month high sampling period during and following Experiment 2 was equal to 125.68 g (2.5% of the total Br\textsuperscript{-} sprinkled), while the amount of Br\textsuperscript{-} export in the downstream site was equal to 201.01 g (4.0%). The specific contribution to stream flow during periods of discharge similar to those during the experimental sprinkling (Table 7), estimated using discharge measurements upstream and downstream from the hillslope (total reach length of 10 m), is 0.22 ±0.14 L s\textsuperscript{-1} (manuscript in preparation).
Figure 20. Scatterplot of the bi-weekly data of 2014 and 2015. Left column: relationship between GW3 and SW Cl\(^-\) (a), SW Cl\(^-\) and discharge (b), GW3 Cl\(^-\) and depth (c), GW3 Cl\(^-\) and EC (d). On the right, in green, the same relationships are shown for Br\(^-\) (e to h).
4.5.3 Velocity estimates derived from the applied tracers

Estimates of maximum velocity were derived using the double EC peak on the last 2 days of Experiment 1 (Section 4.4.2.4). Such estimates were equal to $238 \times 10^{-3}$ m h$^{-1}$ (April 9$^{th}$) and $208 \times 10^{-3}$ m h$^{-1}$ (April 10$^{th}$).

The maximum velocity estimated from the start of EC rise at GW3, a few days after the sprinkling, was equal to $191 \times 10^{-3}$ m h$^{-1}$. The velocity estimated for the peak EC in the well corresponded to $98 \times 10^{-3}$ m h$^{-1}$. On the falling limb of GW3 EC plume, the stream EC described in Section 5.1 was used to estimate a measure of the arrival of the maximum velocity and the mean velocity in connection with the groundwater system, equal to $17.0 \times 10^{-3}$ m h$^{-1}$ (start of raise) and $15.0 \times 10^{-3}$ m h$^{-1}$ (corresponding to stream EC peak).

In 2014, the velocity derived from detecting Br$^-$ in SW in the biweekly samples ranged between 16.0 and $14.1 \times 10^{-3}$ m h$^{-1}$ (calculated respectively for Br$^-$ detected on August 06$^{th}$ and the previous sample on July 24$^{th}$). In 2015, velocities ranged between 4.9 (March 12$^{th}$, during Experiment 2) and $2.7 \times 10^{-3}$ m h$^{-1}$ (December 3$^{rd}$, the last sample where Br$^-$ was detected).

4.5.4 Celerity estimates derived from sprinkling and natural events

Figure 21 shows the box plot of each celerity indices estimated using discharge and water table response timings (Section 4.4.2.5). Celerity values more than 3 standard deviations above the mean are indicated by red crosses and their event number. Event celerities were equal to $19.6 \pm 15.2$ m h$^{-1}$ ($C_{su}$) and $15.2 \pm 21.8$ m h$^{-1}$ ($C_{ss}$), while hillslope celerities were equal to $89.8 \pm 106.2$ m h$^{-1}$ ($C_{wu}$) and $25.2 \pm 34.3$ m h$^{-1}$ ($C_{ws}$) (Figure 21). $C_{wu}$ values were overall much higher than the other estimates, with a maximum of $450$ m h$^{-1}$ for event 3 (Figure 21).
Figure 21. Box plots showing the range of celerity values obtained for the 21 rainfall events. The x axis shows the celerity type, respectively $C_{su}$, $C_{ss}$, $C_{wu}$, and $C_{ws}$. On each box, the central red mark is the median, the edges of the box are the 25th and 75th percentiles, whilst the black sides show the 5th and 95th percentiles. Red crosses indicate difference >3 standard deviations, with outlier events numbered according to Table 2.

Figure 22. Estimates of $C_{su}$ (a), $C_{ss}$ (b), $C_{wu}$ (c) and $C_{ws}$ (d) plotted against each event’s intensity rate (total rainfall divided by the duration of the event). Filled circles indicate events occurring in the winter (wet) period, while empty circles show summer (dry) period events. Outlier events are numbered according to Table 6.
4.6 DISCUSSION

4.6.1 How are groundwater and streamflow dynamics related to rainfall inputs?

The artificial sprinkling experiments did not generate significant hydrometric responses in the GW3 or SW, due to the small amount of sprinkled water on the plot relative to the upslope hillslope area (Section 4.5.1).

Hydrometric responses in this catchment are comprised of an initial discharge peak coinciding with incident precipitation. Depending on antecedent storage conditions, this peak can occur independently or concurrently with a large, secondary peak - referred to as a double-peak response (Martínez-Carreras et al., 2016). During single-peak events (rainfall > 15 mm), SW discharge peaked in less than 1 h, while the water table measured at GW3 reacted after the discharge peak. At the same time, maximum cross-correlations between rainfall and discharge in single-peak events were always less than the maximum cross-correlations between rainfall and water table (Table 6), indicating that discharge and rainfall were better correlated during single-peak events greater than 15 mm. The delayed hillslope runoff response, relative to that of streamflow, has been observed in other studies (Weyman, 1970; Harr, 1977; Turton et al., 1992; Montgomery et al., 1997; Penna et al., 2015). This suggests a complexity in the groundwater response time in comparison to discharge, and suggests delayed recharge to the water table from the unsaturated zone over most of the catchment area – except perhaps in near saturated riparian areas (considering that the peak is indeed primarily event water as proposed by Jackisch et al., 2016; Wrede et al., 2015).

The cross-correlation analysis suggests that the hillslope response in some cases may be controlled by a storage threshold rather than rainfall characteristics (Tromp-van Meerveld and McDonnell, 2006; Graham et al., 2010a; Gannon et al., 2014). The computed cross-correlations using time-series from double-peak events show that there is a mechanism of release of water that is activated when the depth to groundwater reaches to within 1.6 - 1.5 m of the soil surface for rainfall events of more than 15 mm. Above this limit, the water table triggers a connection to the
stream within a time frame of 1 to 3 h. Such connection is demonstrated by the correlation of the second, lagged discharge rise to water table dynamics, characterised by correlation coefficients of 0.90-0.98, rather than to rainfall. Such cases could be defined as storage-driven discharge peaks, and correspond to the second type of peak response described in Martínez-Carreras et al., (2016).

In the case of the storage-driven double-peak events, cross-correlation analysis suggests the first peak can be seen as rainfall-driven, as the maximum correlation to rainfall is similar to correlation coefficients among single-peak events (Section 4.5.1). Some events exhibit a general poor correlation among rainfall, discharge and water table dynamics (event 12 and 21, double peak events characterised by long rainfall duration and low intensity, Table 6); this is likely due to composite rainfall-driven and storage-driven discharge peaks, which are more difficult to evaluate with the cross-correlation technique.

The rising of the water table at the hillslope base concomitantly – or before – discharge increase is the common perception of hillslope groundwater contribution (Mosley, 1979; Sklash and Farvolden, 1979; Kim et al., 2004). The different temporal response observed here between groundwater and streamflow in the rainfall-driven and storage-driven peaks is a non-linear hillslope response (McGuire and McDonnell, 2010) and helps demonstrate the dependence of runoff on storage as shown in Martínez-Carreras et al. (2016). The complex response between precipitation and discharge may be explained by an hysteretic pattern between the hillslope and catchment runoff (McGuire and McDonnell, 2010), suggested in Martínez-Carreras et al. (2016).

4.6.2 Tracer transport between plot and stream

4.6.2.1 Groundwater response

The amounts of Cl⁻ and Br⁻ sprinkled during the 2 experiments were detected in both GW3 and SW at different times (Section 4.5.2). In GW3, a rise in water table corresponded to a decrease in EC, indicating dilution, whilst a decrease in water table corresponded to a rise in EC value, indicating higher concentrations (Figure 18).
The tracers stored in the subsurface are likely responsible for the EC rise in GW3, as EC is an indicator for dissolved ions (Hayashi, 2004). Previous work at the plot scale from soil analysis performed in autumn 2014 (after Experiment 1 was carried out) showed that significant amounts of Cl\(^{-}\) and Br\(^{-}\) stored in the soil were likely remobilised during rainfall events, and that such remobilisation was more pronounced in the case of heavy summer events (Scaini et al., 2017a). An interesting evidence of this behaviour is shown by the third peak in the water table EC (Figure 18.c). During one of the driest months of the series, October 2015 (<30 mm rainfall), the water table level was low (1.9 m below the surface) and stable. Under these conditions, well EC exhibited its highest value for the entire two-year series (207 µS cm\(^{-1}\) on October 23\(^{rd}\)). However, the groundwater level readings between September and November 2015 are suspect of malfunctioning of the instrument, because the water level does not decrease during a period without rainfalls. As the EC of the water table is recorded by the same instrument, we cannot yet make a sound interpretation of this late rise of EC because it might be caused by an instrumental error.

### 4.6.2.2 Stream response

An inverse relationship between EC and discharge linked to dilution was also observed in the stream data and has been documented by others (Kobayashi, 1986). In support of this interpretation, Br\(^{-}\) was detected in the stream measurement points only on low-flow days (Figure 20), when stream chemistry was not diluted with water from rainfall events. The only stream Br\(^{-}\) sample that was detected during high discharge (20.6 L s\(^{-1}\)) was also the only sample containing detectable Br\(^{-}\) and was taken during a rising limb (visible in Figure 19). This event occurred after a long period of low flow (0.31 ±0.25 L s\(^{-1}\)). Unfortunately, stream EC was not available during such a time period (Figure 18).

The reason for stream EC rise during low flows and heavy summer events in 2014 could be due to groundwater fluxes, releasing in the stream the high-EC water containing tracers. In wet conditions, such contribution could be not detected because of its minor contribution to catchment-scale runoff generation, as we do observe little Br\(^{-}\) in the stream during rainfall events. The tracer detection in the
stream only under low-flow conditions does not mean that there is no Br\textsuperscript{−} during high flows. Tracer flux may increase during high flows but the increase may still not achieve concentrations above the detection limit, as this hillslope, with an upslope accumulating area of 3 ha, represents a small fraction of the total catchment area (46 ha).

### 4.6.3 How do bedrock structural properties influence tracer transport from plot to stream?

Recent studies have recognized the importance of identifying runoff generating mechanisms governed by fractured bedrock hydrogeology (Banks \textit{et al.}, 2009; Hale \textit{et al.}, 2016). In the Weierbach, limited information has been available to date to understand the extent that fractured bedrock can influence subsurface flow dynamics. Our set-up allowed us to investigate whether water from the hillslope during events moved along the bedrock cleavage plans or along the predominant slope angle (Figure 15.c). Differences in concentration between the stream sampling points show a clear increase in the downslope sampling points with respect to the sampling point located along the predominant slope angle. This suggests that the predominant flowpath direction follows the bedrock cleavage and not the surface slope. Mass flux estimates of Br\textsuperscript{−} export were higher at the furthest downstream measurement point (4% of input) relative to SW, the stream outlet (2.5% of input); Br\textsuperscript{−} was detected only twice directly downstream from the hillslope (Section 4.5.2).

Unfortunately, the two wells located at the bottom of the experimental plot, GW1 and GW2, were dry throughout the observation period and do not provide useful information other than to further reinforce the heterogeneous nature of the bedrock.

With the available data we cannot query whether the tracer plume moved further downstream than the strike had suggested (i.e. did more tracer reach the stream at angles greater than the bedrock cleavage?). Our data suggest the possibility that groundwater flow was dominated by a downslope gradient different from the surface slope. Such a possibility is described in Figure 23, where arrows
indicate the prevalent flow direction in the soil layer (vertical) and bedrock (laterally oriented fractures, due to cleavage). This 2-layered structure suggests that the deeper groundwater body, within the bedrock, would also cause the catchment area to differ from its topographical approximation. The importance of the subsurface boundaries have been recently discussed in hydrological studies: Hale et al., (2016) identified subsurface permeability structure as the main control on water storage and release. In another study, fractured sedimentary bedrock were responsible for the rapid response of bedrock groundwater at the hillslope scale (Padilla et al., 2014) and resultant generated runoff (Padilla et al., 2015). Pfister et al. (2017) have documented bedrock geological controls on catchment storage, mixing and release in a set of 16 nested catchments in Luxembourg. In our study we could not locate the maximum depth to which groundwater storage extends, but we did manage to identify a structure that controls flow direction through the cleavage orientation, and demonstrated its importance in directing hillslope runoff. In this catchment, a component of flow through the bedrock could also control a larger component of the water balance (as was the case in Panola, Tromp-van Meerveld et al., 2007).

Our hillslope-scale experiment showed that, in the case of fractured systems like the Weierbach catchment, not only bedrock topography but also the cleavage controls the release of water to the stream. Our findings are valid for rainfall events greater than 15 mm, as large amounts of water were sprinkled on a 64 m² plot (Section 4.4.1), during relatively dry antecedent conditions across the catchment. More generally, we suggest that in addition to accounting for flow that occurs at the bedrock and soil interface, we should also recognize the importance of the cleavage orientation to correctly characterise and predict the fracture contributions to runoff.
Figure 23. Sketch of the studied hillslope indicating the prevalent flow direction following the prevalent bedrock cleavage direction. Tracer arrival to the river shows evidence for a diagonal prevalent direction of flow from the plot.

4.6.4 How does tracer transport relate to estimates of celerities?

Being able to estimate both celerity and velocity responses is an important step toward determining dynamic storage variability, which controls both the hydrometric
stream flow response, and the storage that regulates solute transport (Beven, 2012a; Birkel and Soulsby, 2015; Davies and Beven, 2015).

Hillslope celerity estimates for natural rainfall events were equal to 89.8 ±106.2 m h$^{-1}$ ($C_{wh}$) and 25.2 ±34.3 m h$^{-1}$ ($C_{ws}$), while the event celerities were equal to 19.6 ±15.2 m h$^{-1}$ ($C_{su}$) and 15.2 ±21.8 m h$^{-1}$ ($C_{ss}$) (Figure 21). The integral responses were characterised by values within the 25th and 75th percentiles, except for a few cases with exceptionally high values, while the initial estimates were more variable, particularly in the hillslope response. The heterogeneity of our celerity estimates reflects the complexity of the response of the catchment (Figure 21 and 22). The differences between initial and integral response of our estimates, refer to the combination of different processes that are likely involved in the responses (Reeves et al., 1996; Iorgulescu et al., 2007; McDonnell et al., 2010).

The highest celerities, observed during events characterised by high intensity and short duration, were observed during June and July of 2014: events 3, 4, 7 and 8 in Table 6 (Figure 21). The highest celerities corresponded to summer events where the intensity rate was the highest, suggesting an influence of both event intensity and residual storage (summer, warm conditions) on celerity responses. In such a system, a higher rainfall rate would generate a faster response in the unsaturated zone once a storage threshold has been exceeded, resulting in a quicker celerity. The importance of unsaturated zone dynamics in the hydrologic response was suggested in early studies in permeable soils (Torres et al., 1998) and could explain the maximum initial celerities being higher than the integral celerities (Barnard et al., 2010). We observed a seasonality effect in the intensity rate/celerity response of Figure 22: a 20-mm event in summer generates a higher impact on the residual storage of water than the same intensity in winter, as such water quantity would be diluted within the (higher) winter residual storage. In turn, antecedent conditions (in terms of API7, API30 and antecedent moisture) of the correspondent rainfall event did not contribute to explain the high celerity values.

The hillslope setup included continuous measurement of water table depth and streamflow as well as EC monitoring and water sampling allowing for a comparison between velocities and celerities. In comparison to the celerity, the maximum
velocity values (indicated by a grey dotted line in Figure 21) were always below 1 m h\(^{-1}\), in the same range of the lower celerities derived from the natural events (equal to 0.9-1.1 m h\(^{-1}\)).

Shallow lateral preferential flow was observed in the work of Scaini et al. (2017), where maximum vertical velocities estimated for the tracers were variable and ranged as high as 677 ± 420 \(\times 10^{-3}\) m h\(^{-1}\), whilst celerities were as high as 971 ± 625 \(\times 10^{-3}\) m h\(^{-1}\). At the plot scale, the highest measured maximum velocity was equal to 1.2 m h\(^{-1}\). Here, we estimated the maximum velocities at the hillslope scale, as estimated by the two EC peaks recorded in SW (238 and 208 \(\times 10^{-3}\) m h\(^{-1}\)), and found that they are higher than maximum velocity in GW3 (191 \(\times 10^{-3}\) m h\(^{-1}\)), suggesting possible preferential flow pathways (section 4.5.3 and 4.6.1). The EC peaks are not high in magnitude, as increase in EC to 74.5 would correspond to a concentration of Cl\(^-\) of 4.09 mg L\(^{-1}\) (Section 4.4.2.3), and do not suggest a significant volume tracer reaching the water table (though no sample was available on those dates). These maximum velocities suggest that preferential flowpaths may allow for the hillslope to contribute to the first peak. Under the experimental conditions (dry antecedent conditions, and artificial sprinkling on the 64 m\(^2\) plot only, Table 7), it is possible that preferential flow along the hillslope may not reach deep enough to instigate a downslope response (see for example, Germann, 2014).

The estimate of maximum velocity to the stream following the groundwater well peak, \(V_{\text{max,ws}}\), both estimated by EC data (17.0 \(\times 10^{-3}\) m h\(^{-1}\)) and Br\(^-\) detection (14.0 and 16.0 \(\times 10^{-3}\) m h\(^{-1}\)) were in agreement with each other given the sparse sampling interval (Section 4.4.2.4). The movement of tracer in the soil is complex, with Br\(^-\) involved in remobilisation processes (Scaini et al., 2017a), as demonstrated by the high-sampling stream set-up during and after Experiment 2. Additionally, we only calculated sample means, with additional issues about (i) flux weighting as we detect concentrations but not fluxes at the well, and (ii) dilution at the stream to concentrations below detection limit (with the possibility of incomplete mixing with the stream water). Such problems in tracing preferential pathways and sources in fractured bedrock systems have been encountered by others (Genereux et al., 1993; Shand et al., 2007).
4.7 CONCLUSIONS

This study analysed the subsurface flow pathways in the Weierbach catchment (Luxembourg). The peculiarity of this catchment is that it is underlain by slate bedrock, which is orientated in a preferential direction. A major focus of this work was to understand the influence of this anisotropy on subsurface processes.

Sprinkling experiments were designed to infer subsurface flow pathways. In particular, tracer concentrations were monitored at multiple sites through the stream and in a well located along the main direction of the bedrock cleavage. Estimates of hillslope and hydrograph celerities were calculated using water table and discharge responses respectively.

Our main research questions are (i) How are groundwater and streamflow dynamics related to rainfall inputs? (ii) How do bedrock characteristic, including orientation of the fractures, influence tracer transport from plot to stream? (iii) How does tracer transport relate to estimates of celerities?

From the combined hydrometric and chemical analyses, we managed to provide answers to our specific questions.

- For natural rainfall events of more than 15 mm there is a difference between the mechanisms controlling the rainfall-driven (single or first peaks in double peak events) and storage-driven (second peak in double peak events) discharge peaks, supporting recent work undertaken by Martínez-Carreras et al. (2016). Our results suggest that rainfall rate and residual storage present a seasonality effect and are the primary controls on celerity responses.

- The characteristics of our site suggested that bedrock structural properties as cleavage orientation control flow direction, as subsurface flowpaths were in line with the orientation of the bedrock fractures.

- Combining velocity and celerity estimates we suggest that there could be a fast flowpath component connecting the hillslope to the stream, but
velocity information was too scarce to support such a hypothesis, as velocity estimates were largely lower than celerities.

This study has proven the importance of fracture orientation in subsurface flow generation in forested catchments. In particular, cleavage orientation is important in determining the catchment area contributing to runoff, which may differ significantly from the contributing area determined based on topography.
5 FOLLOWING TRACER THROUGH THE UNSATURATED ZONE USING A MULTIPLE INTERACTING PATHWAYS MODEL: IMPLICATIONS FROM LABORATORY EXPERIMENTS

ABSTRACT

Models must effectively represent velocities and celerities if they are to address the old-water paradox. Celerity information is often available, while velocity information is more difficult to measure and simulate effectively, requiring additional assumptions and parameters. This study represents soil profile velocities using the Multiple Interacting Pathways (MIPs) model and validates the representation of velocities with laboratory tracer experiments using structurally intact soil. Despite known properties of soils and tracer influence on them, we are often lacking information on the influence of soil properties on tracer mobility. Undisturbed soil column experiments indicated that the soil microstructure was modified during the experiment. This study features an experimental and modelling approach directed to the evaluation of different structures in the MIPs model, and in particular testing how (i) testing the presence of immobile storage, (ii) varying the shape of velocity distribution, and (iii) testing the transition probability matrices (TPM) influence the model performance. In MIPs, the TPM controls how the modelled water particle velocities are selected from a distribution. MIPs was able to provide a good representation of the experiment. The use of a TPM improved the capacity of the model to predict the tracer breakthrough, and showed that the connectedness of the faster pathways is important in controlling the percolation of water and tracer through the soil. This study shows that the adaptive strategy of the MIPs model has the potential to improve our understanding of soil structural processes through the use of transition probability matrices.

Contribution: I was responsible for designing and executing the column experiment, collecting and analysing the data, and writing. I partook in designing and implementing the model formulation and results.

Based on: Scaini A, Amvrosiadi N, Hissler C, Beven KJ. Following tracer through the unsaturated zone using a multiple interacting pathways model: implications from laboratory experiments. In preparation.
5.1 INTRODUCTION

Tracer velocities, a direct reflection of how quickly pore-water moves through the soil profile, are different from celerities, which are a measure of how quickly the storage of water responds to a rainfall event (Beven, 1989b, 2012a). Differences between velocities and celerities are thought to explain the rapid runoff of stored water during rainfall events (McDonnell and Beven, 2014), and therefore provide an explanation for the old-water paradox (McDonnell, 1990; Kirchner, 2003). However few tracer studies have analysed in situ velocities and celerities to test the interplay between these variables (Mosley, 1982; Öztürk and Özkan, 2002). Moreover, while soil structure is expected to control subsurface flowpath and hydraulic response, how that structure relates to velocity distributions, including preferential flows, is not well understood (Beven and Germann, 2013). Here, we seek to assess the influence of soil structure on water velocities, as inferred from using a particle-tracking model – the Multiple Interacting Pathways (MIPs) model.

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, 1998; Lin, 2010b). The term ‘preferential flow’ encompasses all the processes that occur in non-uniform soils where some part of the flow through the soil bypasses parts of the matrix (Beven and Germann, 1982, 2013). The ways in which the occurrence and characteristics of preferential flow influence the infiltration of water and solutes through the soil is still not well understood.

Time-variant transit-time distributions and novel modelling techniques attempt to analyse the velocity/celerity interplay (Laine-Kaulio et al., 2014; Soulsby et al., 2015; Scudeler et al., 2016) but are often focused at hillslope and catchment scales and thus are unable to directly address the role of soil structure on subsurface velocities. Particle-tracking techniques provide a consistent representation of velocities and celerities, by tracking water properties through the modelling domain (Davies et al., 2011, 2013; Tschiesche, 2012; Maier and Bürger, 2013; Henri and Fernàndez-Garcia, 2014; Zehe and Jackisch, 2016).
MIPs is a particle tracking model, developed to predict both hydrographs and tracer breakthrough curves (Beven et al., 1989). A two-dimensional (2-D) version of the MIPs model has been applied to a covered hillslope located in the Gårdsjön catchment (Sweden). In this catchment, MIPs simulated both flow and tracers concentrations (Davies et al., 2011), was also compared to a kinematic wave approach (Davies and Beven, 2012) and was applied at the catchment scale, in a three-dimensional (3-D) formulation (Davies et al., 2013). MIPs has also been used to show how scale affects flow responses and input, output and storage residence time distributions, as well as the relationship between storage and water table levels hysteresis (Davies and Beven, 2015).

MIPs allows inclusion of a transition probability matrices (TPM), which is a matrix that control exchanges between flow pathways of different velocities, and therefore allow the effects of capillarity, connectivity and preferential processes to be simulated (Davies et al., 2011). Conservative tracer experiments can be simulated in MIPs to explore, through different representations of velocity distributions and the TPM, the occurrence and characteristics of preferential flow processes.

In order to apply the MIPs framework, both fluxes and transport information are required. For most studied catchments, there is usually some knowledge regarding celerity, at least at the catchment scale, since celerity information is implicit in water table, hydrograph, and rainfall-runoff responses. Velocities are more difficult to estimate and require additional assumptions and parameterisations to be estimated. Information on velocity and the residence time of water are commonly estimated through use of geochemical tracers (Harr, 1977; Sidle et al., 1995).

Tracers offer a tool to characterize water velocities and pathways (Trudgill et al., 1983; McGuire and Mcdonnell, 2015). In particular, salt tracers are widely used both at field and laboratory scales due to their high availability, solubility and low cost (Hornberger et al., 1991; Flury and Papritz, 1993; Mortensen et al., 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 (Weihermüller et al., 2007; Abbott et al., 2016). Moreover, tracers are often non-conservative, due to the many processes that can influence tracer
movement in the soil: precipitation and deposition processes, anion exclusion and anion retardation phenomena (Flury and 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 micro-structure (Durst et al., 2013). Solute (and hence tracer) mobility in the soil is linked to leaching, the process of the removal of materials in solution from the soil (Holland, 1996; Stephenson et al., 2006).

Laboratory experiments on solute breakthrough using undisturbed columns (Abdulkabir et al., 1996; Henderson et al., 1996; Reedy et al., 1996; Reeves et al., 1996; Perfect et al., 2001; Akhtar et al., 2004; Yousefi et al., 2014) allow to explore near-natural soil water flow and transport processes under controlled boundary conditions. Handling soil columns, though, is technically complicated and can affect the experiments, due to the introduction of artificial preferential flowpaths, non-ideal injection technique, and unrealistic moisture regimes (Lewis and Sjöstrom, 2010).

This study describes a 1-D version of the MIPs model, aiming at testing the ability of MIPs to reproduce both flow and transport in an undisturbed soil column. By modelling a structurally intact column experiment, hypotheses were made with regard to a) the presence of immobile water, b) the velocity distribution in the soil column, and c) stability of the modelled system micro-structure.

To do so, we describe the study site and soil properties (Section 5.2) and the undisturbed column experiment (Section 5.3). The experiment results (Section 5.4) provide the basis to introduce hypotheses to reproduce the experiment within the MIPs model conceptualisation (Section 5.5). The output from the application of the model (Section 5.6) allows a discussion of inferred soil properties (Section 5.7). The main findings are described in Section 5.8.
5.2 STUDY SITE AND SOIL PROPERTIES

The soil materials used in this study come from the Weierbach, an experimental forested catchment located in the North-West of Luxembourg, underlain by Devonian schist and slate. The altitude ranges from 422 to 512 m a.s.l. The Weierbach catchment has been monitored for its hydro-climatic response for more than 20 years.

The soil is classified as a Dystric Cambisol (Ruptic, Endoskeletic, Siltic, Protospedic) in the World Reference Base (WRB) 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 from a loamy material originated from periglacial atmospheric deposits (Figure 24). The 2C horizon mixes periglacial deposits and slate bedrock residual clasts. The slate clasts increase significantly with depth. 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 investigation demonstrates that the mean saturated hydraulic conductivity increases with depth (Martínez-Carreras et al., 2016). Additionally, the 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).

![Figure 24. Variations with depth of texture properties, i.e. rock, sand, silt and clay contents; sketch of the regolith with larger amount of rock fragments at lower depth. The red box shows the depth at which our column experiment is undertaken.](image-url)
Table 8 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 characterised using soil core data information from site 5 in Martínez-Carreras et al. (2016), the sampling site where the soil and column were extracted. The soil properties were determined with an undisturbed soil core sampler (7.5 cm diameter and 4 cm long cylinder) over 6 replicates per soil layer: bulk density (BD), total porosity (θ), saturated hydraulic conductivity (Ks) and field capacity (FC) were estimated (Table 8). In the Weierbach catchment, θ estimates were rather constant with depth in the first m of soil depth (Martínez-Carreras et al., 2016).

Table 8. Soil properties estimated from core samples replicates, determined as in Martínez-Carreras et al. (2016). Bulk density (BD) was determined by the ratio between the soil dry weight (soil dried at 105°C for 48 h) and the ring volume of the soil core sampler. Hydraulic conductivity at saturation (Ks), total porosity (P), determined based on the standard relationship between bulk density and particle density, field capacity (FC) (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 parameterisation in MIPs. Error estimates refer to one standard deviation.

<table>
<thead>
<tr>
<th>Soil properties</th>
<th>Ah</th>
<th>Bw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (BD) [g m⁻³]</td>
<td>0.64 ± 0.10</td>
<td>0.87 ± 0.05</td>
</tr>
<tr>
<td>Estimated Total Porosity (θ) [m³ m⁻³]</td>
<td>0.75±0.03</td>
<td>0.67±0.02</td>
</tr>
<tr>
<td>Saturated hydraulic conductivity (Ks) [m day⁻¹]</td>
<td>11.21±10.37</td>
<td>16.31±10.03</td>
</tr>
<tr>
<td>Soil at field capacity (FC) [m³ m⁻³]</td>
<td>0.41±0.05</td>
<td>0.37±0.02</td>
</tr>
</tbody>
</table>

5.3 MATERIALS AND METHODS

5.3.1 Undisturbed column experiment

Four undisturbed columns were extracted from the field site, two of which were in the vicinity of location 5 in Martínez-Carreras et al. (2016) in the Weierbach catchment. The columns were collected by excavating away the surrounding soil using a steel ring as a guide. Then, each column was wrapped in cling film, and a plywood box of 30 x 30 x 30 cm size, open at top and bottom, was placed over the column. The space between the plywood box and the soil block was filled with polyurethane foam and allowed to dry out for one day before moving the columns.
The column bottoms were secured with a piece of plywood and the whole samples were wrapped in cling film for conservation. The cores were then taken back to the laboratory. Three of the columns were employed to perform diatom percolation experiments and dye tracing in comparison with other substrates (De Graaf, 2014). One column was used for infiltration experiments.

5.3.1.1 Experiment setup

In order to perform the experiment under drainage boundary conditions, the column was submerged prior to performing the experiment in water of the Weierbach catchment. It was then left draining on a level plastic support adapted to support the column during the experiments. The top surface was left open to infiltration, and the bottom surface was left open for drainage. Tracing experiments were carried out using NaCl as a tracer.

The pore volume (PV) of the column, defined as the volume of pores that can be filled by water, was calculated using the porosity information calculated on both horizon Ah and Bw on the core samples of Section 2, expressed as total porosity – obtained by multiplying core volume by estimated porosity (Reeves et al., 1996).

The column experiment was performed in a greenhouse sited at the Luxembourg Institute of Science and Technology (LIST) in Luxembourg and lasted a total of 3 days. During the column experiment, the total water applied was equal to 12 L. The phases of the experiment are shown in Table 9. On the first day (Event 1), the column was left on the support until reaching field capacity (i.e. until the outflow collected from the bottom of the column was negligible). 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. Ponding was present, showing that the water input rate had exceeded the infiltration capacity (i.e. the surface soil layer was saturated). 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 such water was percolated, the rinsing phase started. A total of 9 L were used to rinse the column – 2 L on the same day, and respectively 5, divided in 2
events separated by 6 h, respectively Event 2 and Event 3, and 2 L (Event 4) over the following two days (Table 9).

Table 9. Characteristics of the tracer application and rinsing events during the column experiment. Both water applied, expressed in L, and the equivalent pore volumes are provided.

<table>
<thead>
<tr>
<th>Time</th>
<th>Phase</th>
<th>Water applied (L)</th>
<th>Equivalent PV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 1</td>
<td>Event 1</td>
<td>Water</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NaCl solution</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rinsing</td>
<td>2</td>
</tr>
<tr>
<td>Day 2</td>
<td>Event 2</td>
<td>Rinsing</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Event 3</td>
<td>Rinsing</td>
<td>1</td>
</tr>
<tr>
<td>Day 3</td>
<td>Event 4</td>
<td>Rinsing</td>
<td>2</td>
</tr>
</tbody>
</table>

5.3.1.2 Output measurements

Volumes of outflow were measured by weighing samples collected every 5 minutes. All the drainage was collected, but not all the samples were analysed for tracer concentration, because of time available on the analytical equipment. 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 minutes. All collected 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 the samples were analysed, the mass of Cl\(^-\) was estimated by (i) interpolating linearly between the measured points to match the sample timing of the outflow volume; (ii) multiplying Cl\(^-\) concentrations to outflow volume to obtain the load; (iii) summing up all the values to obtain the total mass of Cl\(^-\).
5.4 EXPERIMENTAL RESULTS

5.4.1 Column experiment results

The water application rate at the column surface exceeded the infiltration rate, therefore ponding was observed at the initial stages of all the water application events. During the column experiment, a total of 12 L (1.09 PV) were applied on the surface of the soil column.

The total volume measured for Cl⁻ concentration was 7 L. Using the interpolation technique described in Section 3.1.2, a recovery of 78% in Cl⁻ was estimated, showing that less than one pore volume was sufficient to rinse out a large part of the applied tracer.

A challenging outcome was identified analysing the experimental results: the column experiment showed that Event 1 held more water (as determined from the volume of outflow) than Events 2 and 3, where outflow was greater than input. While the mass balance between the input volume and the retrieved volume showed almost total recovery, reaching 97%, the mass balance did not add up for any of the individual events, as shown in Table 10.

Table 10. Inflow/outflow rate, expressed in %, for each event during the experiment.

<table>
<thead>
<tr>
<th>Time</th>
<th>Inflow</th>
<th>Outflow</th>
<th>Inflow/outflow rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 1</td>
<td>Event 1</td>
<td>5</td>
<td>4.2</td>
</tr>
<tr>
<td>Day 2</td>
<td>Event 2</td>
<td>4</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>Event 3</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>Day 3</td>
<td>Event 4</td>
<td>2</td>
<td>1.8</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>12</td>
<td>11.6</td>
</tr>
</tbody>
</table>
5.4.2 Model hypotheses to be tested

The mismatch between inflow and outflow volumes suggested two possibilities:

(i) Experimental error, due to unaccounted evapotranspiration losses. This possibility was ruled out, on the grounds of minimal estimated actual evapotranspiration rate (1 mm d\(^{-1}\)) at the experiment location, which was not enough to account for the mismatch.

(ii) Modified pore structure or variable moisture conditions causing a variable volume of immobile water storage. At this site, a structural change following a multi-tracer 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 field capacity on moisture conditions (e.g., Kampf, 2011).

Based on this result, in the following sections we present 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 experiment. The model was run using the data from the undisturbed column experiment to test which process representation hypothesis can reproduce the experimental observations.

The following hypotheses were tested:

a) Varying the shape of the velocity distribution can affect both discharge and tracer outputs;

b) The effects of pore connectivity can be characterised by modifying the transition probability matrix (TPM);

c) Water storage can be effectively immobile when it falls below field capacity, 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 5.2.
5.5 MIPS FORMULATION

5.5.1 Modelling conceptualisation and requirements

In this study we used a 1-D MIPs model, with velocities driven by gravity, representing the free-draining column, and able to capture the ponding at the surface of the column for the cases when precipitation exceeded the infiltration rate. Such an approach is consistent with the type of Stoke’s flow representation of water movement under gravity suggested by Germann (2014) and (Beven and Germann, 2013). MIPs represents water within the soil system as a large number of particles (here particle volume equals to 1 mL), which move through the system with velocities randomly selected from a pre-defined velocity distribution. 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 minutes).

In the original MIPs model (Davies et al., 2011, 2013), given an infiltration rate, the velocities of water particles in the unsaturated zone were dependent on the moisture content that would be reached through that infiltration rate, if applied constantly. Here this assumption was kept only for the newly added particles, while 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 at each time step.

In the model representation the column was split into 1 cm thick layers. At each time step the water content (w) of each layer was calculated, and used to produce the velocity distribution within that layer, assuming an exponential distribution of velocities (Equation 1) as in previous applications of MIPs (Davies et al., 2011, 2013):

\[ v = v_0 \cdot \exp(b \cdot w \cdot R) \] (1)

where \( v_0 \) is the minimum pore water velocity, \( b \) is a parameter defining the skewness of the distribution, and \( R \) is a vector with uniform random distribution and length equal 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 \( w \) 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 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.

For the case of saturation \( w \) would be equal to porosity (\( \theta \)), and the integral of unit gradient velocities would equal to the vertical saturated hydraulic conductivity \( K_s \) (Equation 2).

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

(2)

From this equation \( \theta \) can be derived as a function of \( K_s \), \( v_0 \) and \( b \). For each model run, aiming at keeping \( \theta \) within the measurement range, two combinations of parameters \( v_0 \) and \( b \) were obtained by manual calibration. Two velocity distributions (more and less skewed) resulted from the respective two parameter combinations: \( v_0 = 1 \text{ mm} \cdot d^{-1}, b = 17.9 \), and \( v_0 = 1 \text{ cm} \cdot d^{-1}, b = 14 \).

In all the model versions used for the hypotheses testing, the initial moisture content was set within the limits of measured field capacity. At the upper boundary, infiltrating particles were assigned velocities consistent with the exponential velocity distribution and controlled by the infiltration rate. When the surface was ponded, the full velocity distribution equivalent to the saturated hydraulic conductivity (as in Equation 2) was used. For inputs of tracer solution, each particle was labelled with an equal mass of tracer. The model was first run with parameters \( v_0 \) and \( b \) chosen so that the porosity remained within the measurement range. To examine the effect of pore-water velocity distribution on discharge and tracer transport (i.e. hypothesis (a)), the model was run with the two velocity distributions described above.

The hypotheses regarding the soil micro-structure and pore connectivity, hypothesis (b), was examined by employing the TPM, and comparing the modelled and measured Cl⁻ output. The role of the TPM is to control how the water particles exchange their velocities while they travel through the soil. In the case where 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. Below this set-up will be called high exchange scenario (Ex_H). When TPM was specified, the probability to exchange velocity was adjusted so that the water particles would tend to retain their velocities. Below this case will be referred to as the low exchange scenario (Ex_L).

In the work of Scaini et al. (2017) the high velocities observed at the plot scale were also associated with pore continuity (Yousefi et al., 2014). With Ex_L we simulate different scenarios of velocity to relate it back to the pore continuity, as we assume that (i) if a water particle was travelling along a macropore (and therefore had high velocity), the probability for it to keep moving along this macropore and not infiltrate into smaller pores was high, and (ii) the length of the pores was on average longer than what a particle could cover within a time step.

All the particles of each layer were split in three velocity classes: slow, medium and fast. The classes were also a result of manual calibration; the 40% slowest particles were included in the slow class, the fastest 50% particles in the fast class, and the intermediate velocities belonged to the medium class. The probabilities to change from one class to another (i.e. TPM) were set according to two rules: (i) the sum of probabilities for a particle to be found in any class during a time step is 1 (i.e. the sum of each row and column is 1); (ii) the particles have lower probability (10% chance) to move to a different velocity class, and higher probability (80% chance) to stay in the same velocity class (Table 11).

Table 11. 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).

<table>
<thead>
<tr>
<th>From:</th>
<th>Slow</th>
<th>Medium</th>
<th>Fast</th>
</tr>
</thead>
<tbody>
<tr>
<td>To:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slow</td>
<td>80</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Medium</td>
<td>10</td>
<td>80</td>
<td>10</td>
</tr>
<tr>
<td>Fast</td>
<td>10</td>
<td>10</td>
<td>80</td>
</tr>
</tbody>
</table>
Finally, in order to identify a model that would predict well both the discharge and Cl\textsuperscript{−} export, a manual calibration was performed again, in this case allowing the parameters to vary beyond their measured limits.

For the cases of velocity distribution (hypothesis (a)) and velocity exchange probability (hypothesis (b)), early 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 would have required additional parameters (e.g. location of immobile particles, exchange rate and efficiency between particles). A simpler solution was tested instead: particles within a layer with soil moisture below field capacity were given zero velocity (hypothesis (c)). This approach allows the proportion of immobile storage to vary in time and produced satisfactory results with only one additional parameter – the field capacity. The immobile storage approach is justified on the basis that the slow rates of drainage below field capacity are the product of both low relative hydraulic conductivities (reflected in the exponential velocity distribution), and capillary gradients acting against gravity (not explicitly considered in MIPs).

5.5.2 Model evaluation

The modelled discharge and Cl\textsuperscript{−} outputs were evaluated against measurements by calculating the adjusted coefficient of determination, $R_{adj}^2$ (Equation 3) for the cumulative discharge normalized to total input (Equation 4).

$$R_{adj}^2 = 1 - (1 - R^2) \cdot \frac{(N - 1)}{(N - p - 1)}$$ (3)

Where $N$ is the sample size (here $N = 124$), and $p$ is the number of independent variables (here $p = 1$).

$$Q_c = \frac{\sum_{t=1}^{t=N} Q(t)}{\sum_{t=1}^{t_N} I(t)} , \ t = 1, ..., N$$ (4)

where $I(t)$ is the input per time step and $N$ is the total number of discharge measurements.
To evaluate the Cl\textsuperscript{−} export, the cumulative and normalized to total Cl\textsuperscript{−} input, corrected for the initial Cl\textsuperscript{−} content, was used (Equation 5).

\[
Cl_{c}^{-} = \sum_{t=1}^{t} Cl_{out}^{-} (t) \div \left( \sum_{i=1}^{N} Cl_{in}^{-} (t) + Cl_{init}^{-} \right)
\]  \hspace{1cm} (5)

where \( Cl_{in}^{-} \) is the Cl\textsuperscript{−} input (mg) at every time step, and \( Cl_{init}^{-} \) is the initial Cl\textsuperscript{−} content in the soil column.

Both \( Q_{c} \) and \( Cl_{c}^{-} \) were used to evaluate the different tested hypotheses. Three scenarios were analysed: (i) no immobile water, more skewed velocity distribution, (ii) no immobile water, less skewed distribution, and (iii) immobile water assumption. These three scenarios were tested for both Ex\textsubscript{L} and Ex\textsubscript{H}.

### 5.6 MIPS RESULTS

#### 5.6.1 Testing the different hypotheses

First, the case of Ex\textsubscript{H} was examined (Figure 25.a). Not allowing for immobile water (blue and yellow lines) resulted in longer drainage times than observed. Since the modelled discharge was calculated for the same time periods as the measurements, the excessive simulated drainage resulted in abrupt offsets in Figure 25 (stepwise behaviour of blue and yellow curves). Changing the shape of the velocity distribution (but always keeping \( \theta \) and \( K_{s} \) constant) showed that the less skewed distribution (yellow lines) allowed for more drainage; the soil water content at the end of this simulation was smaller than the initial one (set equal to measured field capacity), and therefore the curve reached a value above 1. On the other hand, for the case of no immobile water with less skewed velocity distribution, as well as for the case of immobile water with variable field capacity, \( Q_{c} \) reached exactly the measured value (0.96). The adjusted coefficient of determination increased from 0.92 to 0.98 with the assumption of immobile water (orange line, Figure 25.a).

The recovery of Cl\textsuperscript{−} for all the three cases mentioned above was 88%, which was higher than the measured 78% (Figure 25.b), and their \( R_{adj}^{2} \) was also similar, ranging between 0.83 and 0.85.
Figure 25. Scenarios without transition probability matrix. Cumulative normalized discharge (a) and cumulative normalized Cl\textsuperscript{-} export (b) against time, for the time steps where the observed discharge (Q(t)) was greater than zero. Black lines: measured values; blue lines: scenario with no immobile water, and more skewed velocity distribution; yellow lines: scenario with no immobile water and less skewed distribution; orange lines: scenario with immobile water and variable field capacity assumptions. The time of salt application is indicated by a grey area. The grey dashed lines show the beginning of each event. The legend shows the adjusted coefficient of determination of each scenario.

The general behaviour of the scenarios mentioned above was the same after introducing TPM, but the performance was slightly improved in comparison with Figure 25.a (Figure 26.a). The Cl\textsuperscript{-} export was still overestimated with respect to the measured, particularly for Events 3 and 4 (Figure 26.b), but the performance of the less skewed velocity distribution (blue line) and the mobile storage assumption (orange line) were slightly improved with $R_{adj}^2$ reaching 0.87.

In both Ex\textsubscript{L} and Ex\textsubscript{H} cases, the scenario that shows the lowest capability in reproducing the experimental data is the mobile water and less skewed velocity distribution (yellow line, Figure 25 and 26). The immobile water hypothesis and the more skewed velocity distribution shows the best fit to both discharge and tracer export, being the most performant in all scenarios, both with Ex\textsubscript{L} and Ex\textsubscript{H} (orange line, Figure 25 and 26).
Figure 26. Scenarios with transition probability matrix. Cumulative normalized discharge (a) and cumulative normalized Cl\textsuperscript{-} export (b) against time, for the time steps where the observed discharge (Q(t)) was greater than zero. Black lines: measured values; blue lines: scenario with no immobile water, and more skewed velocity distribution; yellow lines: scenario with no immobile water and less skewed distribution; orange lines: scenario with immobile water assumption. The grey dashed lines show the beginning of each discharge event. The legend shows the adjusted coefficient of determination of each scenario.

5.6.2 Best model performance

In an effort of improving the fitting of the Cl\textsuperscript{-} export also for the last part of the experiment (Event 3 and 4) we explored the option of a changing pore system: we allowed for changes in field capacity, resulting in the value of saturation required to have immobile water to be changing with time.

When the parameters were selected so that porosity was allowed to vary beyond its measurement limits, the best fit obtained by manual calibration was achieved for $v_0 = 1 \text{ cm} \cdot \text{d}^{-1}$ and $b = 12.5$ resulting in $\theta=0.71$, with $\text{Ex}_L$, and with velocity classes defined as: slow, equal to the slowest 40% and fast, equal to the fastest 10%. The field capacity (varying between 0.28 and 0.42 m$^3$ m$^{-3}$) was kept exactly the same as in the immobile water scenario described in section 6.1. The adjusted coefficient of determination for this case was 0.99 both for $Q_c$ and $Cl_c$ (Figure 27.a and 27.b respectively).
5.7 DISCUSSION

Undisturbed soil column experiments are often used to analyse soil properties in response to addition of salts in natural soils. Even in such controlled conditions, analysing the changes in soil structure is a challenge – despite the possibility of thin-layering the column (Bouma et al., 1977) or performing 3-D imaging and X-ray tomography (Anderson et al., 1990; Wildenschild et al., 2002; Luo et al., 2010; Garel et al., 2012).

In our column experiment, only about one pore volume in total was used over all the applications (Section 5.3). The observed shift in the response from Event 1 (the first day) and the other 2 days of rinsing the applied salt (Event 2, 3 and 4) suggested that some pore structure, and consequently the field capacity, changed during the experiment – and was observed both in this study and in the field study of (Scaini et al., 2017a). Early studies showed significant retention of tracer in undisturbed cores, despite the application of more than 4-5 pore volumes of water (Abdulkabir et al., 1996), and other studies proved that hydraulic conductivity decreases in correspondence of an increase of Cl\textsuperscript{-} concentration in laboratory conditions.
(Devrajani, 1993). Not having information on such complex processes, we tested different hypothesis that could help understand the measured change in pore structure after the salt application. Below, we discuss the hypotheses tested with MIPs in order to understand this behaviour.

5.7.1 Time variable immobile storage improved the model performance

The immobile water hypothesis, hypothesis (c), was explored by preventing water particles to move when local layer water content falls below the value of field capacity (Section 5.5.1). This allows for the retention of tracer, without introducing any additional parameters. The immobile water option was important in improving the volume performance, even though it was high for all the models, with adjusted coefficient of determination that increased from 0.92 to 0.98 with the assumption of immobile water. The tracer recovery was overestimated (88% vs the 78% of the measured) by all the hypothesis tested (Figure 25 and 26), and despite $R^2_{adj}$ ranging between 0.83 and 0.85, the dynamic of Cl$^-$ export was not well represented (Section 5.6.1).

Despite the good performance of the discharge for all the studied cases, the best performance was obtained with the inclusion of the immobile storage. 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 overestimated). This suggests that some additional retention mechanism is required: either to increase exchange with fully immobile storage or some geochemical process. Either will require additional parameters to be specified. Apparent changes in soil structure (discussed below) might suggest the need to include more geochemical processes.

5.7.2 The shape of the velocity distribution influenced discharge output

The combination of parameters chosen, all within the measurements bounds of Table 8, showed that the skewness of the shape was important – i.e. the shape of the velocity distribution showed a better performance in the more skewed case. More drainage was allowed in the less skewed velocity distributions, while the more skewed reproduced correctly the cumulative outflow. This was because in the case of less skewed velocity distribution, the minimum allowed pore water velocity ($v_0$) was
higher than in the case of more skewed distribution. This results in the slowest possible pore water to be more mobile in the case of less skewed velocity distribution, and therefore more drainage was observed (Figure 25). The fact that $Q_c$ ended up being more than 1, could be an indicator that the actual minimum pore water velocity in the soil column was less than 1 cm day$^{-1}$.

The fact that velocities are exponentially distributed, and that velocity and pore size are interconnected has been shown before (Beven and Germann, 1981; Germann and Beven, 1981; Siena et al., 2014). Initially, using various velocity distributions was a hypothesis to be tested, but later it showed that there is not much difference in which distribution we use, given that the distribution has to be skewed, and truncated so that $\text{mean}(v) = K_s/\theta$. Other cases with even more skewness of the parameters of the exponential, and a log-normal velocity distribution were also tested (data not shown), but did not help to reproduce all the events. We could not get to find a parameter set that would solve this problem without introducing persistence in particle velocities using the TPM.

5.7.3 The hypothesis of velocity persistence improved tracer simulation

The use of the TPM allowed examining two extreme cases: exchange at every time step, and almost no exchange (Section 5.5.1). Conceptually this would mean that there was small exchange between slow and fast pathways, and that the pore size had high spatial autocorrelation (Section 5.5.1), as presented in the work of Gerke and van Genuchten (1996). Handling persistence could be done correlating velocity from one time step to another, but by using two extreme cases of the TPM we allow different persistence in slow and fast classes in a more consistent framework.

The differential persistence in the different classes, represented by the use of the TPM, 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 field capacity. The difference between these two extreme cases of connectivity ($\text{Ex}_L$ and $\text{Ex}_H$) cases shown in Figure 25 (left and right panels respectively) lies in different ways of incorporating persistence. With $\text{Ex}_H$, the particles were allowed to exchange
their velocity at each time step, without any dependency between former and latter velocities. This can be described as fast exchange between flowpaths, and could represent a structure where the spatial correlation of the pore size is very small. With $\text{Ex}_\text{L}$, a restriction was added regarding the possible velocities to be selected at the next time step, as the fast, slow and intermediate particles were given a specified probability to remain in the same velocity group or move to another velocity group. This could be interpreted as an increase in spatial correlation of velocity; all the particles were assigned an 80% probability to remain in their velocity class, and only 20% probability to move to another velocity class.

Following the discussion above, the observed improvement in the simulation of $\text{Cl}^-$ output using the TPM (always referring to the case where immobile water was allowed) could be attributed to a more realistic representation of the soil column micro-structure. This concept is explained in Figure 28, where the column using 10 dotted lines representing the pores is represented in the 2 different extreme cases hereby analysed: with $\text{Ex}_\text{H}$, flowpaths are short and not interconnected, as each particle changes velocity at each time step (Figure 26.a). In this case, the average length that a water particle would cover during a time step of 1 min would be $\sim$6 mm. With $\text{Ex}_\text{L}$ the particles tend to keep their velocities; in this case the average distance covered by fast particles per time step would be $\sim$12 mm (red), and $\sim$0.1 mm by slow particles (blue).

Our tests show that in the end it is not only the macropores, but also how such macropores allow processes of water exchange and connectivity, that matter in reproducing the experiments. It is known that often connectivity allows or denies the possibility of connectedness of the macropores (Beven and Germann, 1982). It is not enough to know the structure of the soil, it is also critical to understand which processes are involved (Jarvis, 1998; Lin, 2010b). After all, many different types of preferential flows can be occurring at the same time, including finger flow, bypass flow, macropore flow (Kung et al., 2000; Gerke et al., 2010; Beven and Germann, 2013; Krzeminska et al., 2013), and our strategy using different TPM show that MIPs has the potential to represent such complexity in an effective way. The TPM, with low exchange between slow and fast pathways, and the pore size have high spatial
autocorrelation, effectively represent the connectedness of the macropores at this site.

Figure 28. Sketch showing the two extreme cases of connectivity. In the example, the average distance that the particles would be covering in 1.5 minutes is shown for 10 particles, 5 slow (blue) and 5 fast (red). (a) In Ex$_H$, macropores are short and not interconnected, as each particle changes velocity at each time step. (b) In Ex$_L$, more pores are connected through the soil space.

5.7.4 The soil micro-structure changed during the experiments

The idea of trying a variable field capacity concept was introduced as none of the tested parameter combinations and distributions were able to reproduce well both the initial and the final stages of the experiment. If the studied system was changing during the experiment, it would be impossible to model it with constant system characteristics. The hypothesis that the soil micro-structure was changing during the experiment can be supported by the variable observed discharge ratios (water in divided by water out).

The ability of MIPs to represent time-varying local immobile storage was then improved by allowing for a variable field capacity parameter in the model, adjusted outside the measurement bounds of Table 8. A change in field capacity allowed the totality of the experiment to be reproduced, not only one part of it (Figure 27).

The changes in field capacity correspond to a conceptual idea rather than based in Darcian physics (Section 5.7.1), but was tested here on the basis of a change of soil properties in time, which was suggested in previous work where a decrease in infiltrability characteristics was observed after application of NaCl in concentration of...
5 g L\(^{-1}\) (Scaini et al., 2017a). The change in field capacity was motivated by the fact that we were not accounting for the addition of salt tracer used in the experiments, which might cause a number of processes to affect soil structure (Holland, 1996; Gharaibeh et al., 2009). The presence of sodium in the percolating solution or in the ion-exchange complex frequently has been observed (qualitatively) to decrease permeability (Rengasamy and Olsson, 1991). Some studies on loamy-sand soil showed that a five-fold rise in electrical conductivity generates an increase in the exchangeable cations, responsible for an increases in dissolved organic carbon (DOC) sorption processes (Setia et al., 2013). Early studies demonstrated that (i) 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 and Shainberg, 1979), and (ii) such “salt-dependency” of hydraulic conductivity could be modelled on salt water intrusion events (Mehnert and Jennings, 1985). Other study supported such structural changes exploring the effects of salt-dependency on different textures and aggregates sizes (Ben-Hur et al., 2009) and demonstrated the process of clogging of macropores under saline conditions (Basile et al., 2012). Leaching of NO\(_3\)-N and atrazine was observed to increase with increase in salt concentrations (Devrajani, 1993).

This change in micro-structure could be supported by the lower amount of Cl\(^-\) exported in the experiment compared to the modelled under all tested hypotheses (Figure 25.b, 26.b). The mass of Cl\(^-\) exported during the experiment, a total of 78% of the Cl\(^-\), showed that the 22% that was somehow retained would reflect such an important change in micro-structure. In support of this, we observed a visible change of slope in the outflow during the Event 1, likely causing clogging in some of the more surface pores and modifying the micro-structure of the upper layer due to swelling of the clays (in this soil, about 20-25\%, Section 5.2). Such greatest initial modification is expected in earlier events and expected to be smoothed down after further applications, and could be the reason why during Event 4 the slope was reduced to pre-salt experiment.

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

5.8 CONCLUSIONS

Simulation of both hydrograph (celerity response) and tracer breakthrough (velocity response) is one important step to make in order to solve the old-water paradox. Tracer movement through the soil is the most useful way of 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 field capacity, during the experiment. Three hypothesis were tested with MIPs by (i) varying the shape of velocity distribution, (ii) testing the transition probability matrices (TPM), and (iii) testing the presence of immobile storage.

MIPs provided a good representation of the volume outflow during the experiment. The outcome of the three tested hypothesis showed that:

(i) the use of a more skewed velocity distribution improved the ability to reproduce the evolution of the pore structure;

(ii) the use of the TPM 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.

(iii) the best model performance was obtained with the inclusion of a time-varying local immobile storage;

None of the tested parameter combinations and distributions were able to reproduce well both the initial and the final stages of the experiment. The ability of MIPs to represent immobile storage was improved by allowing for a variable field capacity parameter in the model, which allowed the totality of the experiment to be adequately reproduced.
ABSTRACT

This study proposes a framework for estimating both vertical and lateral celerities at hillslope and catchment scales. In an analysis of 198 rainfall events, we explore the relation of groundwater and discharge response times to wetness indicators and evaluate how vertical and lateral celerities are related across the catchment. In response to rainfall, discharge tends to react quickly, in 70% of the cases earlier than groundwater. This holds also for two wells located at the bottom of the hillslopes, which show on average a delayed response relative to discharge. Antecedent conditions metrics including storage deficit do not show a clear relationship to groundwater response metrics. Celerity information estimated by using lag to rise, as well as lag to peak, is useful in understanding complex interactions between groundwater and discharge response during natural rainfall events. The velocity/celerity estimates showed a linear relationship between the streamflow peak celerity and the corresponding velocity. We found that small rainfall amounts could induce rapid lateral flow even without generating a high rise in the water table. This suggests that a small pore volume is sufficient to generate a subsurface response. In catchments dominated by subsurface contributions to the hydrograph, as in the Weierbach catchment, lag time and time to peak should be defined in terms of celerities rather than water flow velocities, and traditional lag time and time of concentration should consequently be revisited.

Contribution: I was responsible for methodological definitions, data analysis, and writing. I partook in setting up the rainfall events detection algorithm.

Based on: Scaini A, Rinderer M, Beven KJ. Estimation of velocities and celerities using empirical data: from theory to practice. In preparation.
6.1 INTRODUCTION

Recent studies highlighted the importance of differentiating between celerity and velocity to better understand runoff generation processes and transports of nutrients, pollutants and tracers in watersheds. Celerity is defined with respect to the speed with which a perturbation to the flow (i.e. rainfall) propagates through the flow domain (McDonnell and Beven, 2014). Simply put, a celerity is the distance between input and output, divided by the time between input and output response. In hydrology, the inputs are typically rainfalls distributed heterogeneously across the watershed and the output variables are discharge, groundwater rise, soil moisture changes etc. Celerity responses depend on the nature of the perturbation and the antecedent wetness, which in a catchment is determined by rainfall, evapotranspiration and changes in storage.

A major part of subsurface flow contributing to stream flow is generated by diffuse flow processes (Berne et al., 2005), driven by an increase in the pressure head and the resulting translation of a pressure wave that can rapidly propagate through the saturated zone over long distances (Beven, 1981, 1982, 1989; Henderson and Wooding, 1964; Hrachowitz et al., 2013; Lighthill and Whitham, 1955). The streamflow (hydrograph) response is controlled by celerities and the effective storage that is filled and emptied as the groundwater rises and falls (Beven, 2010; McDonnell and Beven, 2014).

Velocities and tracers can contribute to understanding the dynamics of watershed storage (McDonnell and Beven, 2014). The term velocity describes the actual movement of a water molecule (travel distance divided by travel time) either through the matrix or preferential flow paths. The movement of water particles can be tracked by (i) monitoring the properties of water molecules, using water isotopes, (ii) monitoring properties that the water carries within its path, in terms of concentration of solutes, or (iii) with the use of actively introduced tracers (Sklash et al., 1976; Kobayashi, 1986; Kendall and McDonnell, 1998; Rodgers et al., 2004). Velocities are generally smaller than celerities, and in the subsurface will be equal to celerity only in some specific cases of preferential flow (McDonnell and Beven, 2014).
Differences between velocities and celerities are thought to explain the rapid runoff response of stored water during rainfall events (Beven, 1989, 2012; McDonnell and Beven, 2014). Being able to estimate both celerity and velocity responses is an important step toward determining dynamic storage variability, which controls both the hydrometric stream flow response, and the storage that regulates solute transport (Beven, 2012a; Birkel and Soulsby, 2015; Davies and Beven, 2015). Novel model frameworks integrate characteristics of celerity and velocity by considering celerity distributions, which manifest themselves in the hydrograph, and velocity distributions, which manifest themselves in the tracer response (Davies et al., 2011; Laine-Kaulio et al., 2014; Birkel and Soulsby, 2015; Soulsby et al., 2015; Scudeler et al., 2016). However, while average celerities and average velocities can be estimated at catchment scales (Rasmussen et al., 2000), few studies to date have explored their datasets to characterise and link in-situ velocities and celerities (Scaini et al., 2017a).

To quantify both velocities and celerities, a time difference and a distance between a source and a target location are required. While timing differences can often be estimated from the response timing of input and output data, it is much harder to define the appropriate distance for which we should calculate celerity given the distributed nature of the response. Here we propose 2 types of celerity index (vertical and lateral) within a framework that captures the hydrologic functioning of a catchment, linked to in situ observations of soil moisture, groundwater and streamflow. The vertical celerities measure the propagation of a wetting front, as observed at soil moisture profiles and the response of the water table in wells located in flat areas of a catchment. The lateral celerities measure the propagation of a perturbation, mainly from uphill locations to downhill locations, and therefore take into account the contribution of the subsurface storm flow to the well response (hillslope celerity) and to the stream hydrograph (event celerity). This is based on the assumption that the hillslopes are the landscape units that contribute to streamflow (Jackisch et al., 2016; Martínez-Carreras et al., 2016). Celerities can be calculated for both (i) the initial response (time between rainfall start and start of soil moisture, discharge and groundwater table response) and (ii) the peak integral response (time frame between rainfall start and peak of soil moisture, discharge and
groundwater table response). The same framework is applied to estimate velocity information at three sites using electrical conductivity data, as an indicator for dissolved ions (Hayashi, 2004).

Storage-discharge relationships are widely used tools for the description of catchment behaviour (Fenicia et al., 2006; Kirchner, 2009; Teuling et al., 2010; Camporese et al., 2014; Creutzfeldt et al., 2014; Gannon et al., 2014). Complex and hysteretic relationship between storage and discharge have been observed (e.g. Beven, 2006; Davies and Beven, 2015; Norbiato and Borga, 2008) and shown to be controlled primarily by antecedent wetness conditions, seasonal climate variability or surface and subsurface topography (Tromp-van Meerveld and McDonnell, 2006; Farrick and Branfireun, 2014). Groundwater response, often employed to characterise storage fluctuations in time, is however strongly related to where groundwater is monitored within the catchment (Haught and Van Meerveld, 2011; Penna et al., 2015; Rinderer et al., 2016). The response and shape of the relationship between storage and discharge can potentially provide information on the celerity response distributed over the catchment.

In this study we seek to understand the relationship between celerity responses within the catchment and at the catchment outlet, by analysing streamflow, soil moisture and groundwater response at three wells situated in different parts of the Weierbach catchment in Luxembourg. We address the following research questions:

(i) How are groundwater and discharge response times related to wetness indicators?

(ii) How variable are vertical and lateral celerities across the catchment and at the catchment outlet?

(iii) How do in situ velocities and celerities relate to each other?

6.2 EXPERIMENTAL FIELD SITE

The Weierbach, an experimental catchment located in the northwest of Luxembourg, is a 46 ha catchment with altitudes ranging from 465 to 512 m a.s.l., 812 mm year\(^{-1}\) average annual rainfall (2007-2016), and 0.55 annual runoff ratios (average 2005 to 2008) (Martínez-Carreras et al., 2016). The Weierbach is
characterised by steep slopes (on average 10°, 33% of the catchment area) with a flat plateau area on the upper slopes. The land use is characterised by mixed forest composed of stands of *Quercus robur* (Oak), *Fagus sylvatica* (Beech), *Picea abies* (Norway spruce), and *Pseudotsuga menziesii* (Douglas fir).

The catchment is underlain by Devonian slate and is constituted by Pleistocene Periglacial Slope Deposits covering the *in situ* compact and slightly weathered slate bedrock also called saprock (Eggleton, 2001; Juilleret *et al.*, 2011; Martínez-Carreras *et al.*, 2016). The whole regolith classification is Dystric Cambisol (Ruptic, Endoskeletic, Siltic, Protospodic) according to the World Reference Base (WRB, 2015) overlying a Regolithic Saprock (Vertifractic, Rootic) [Slastic] (Juilleret *et al.*, 2016).

The Weierbach is characterised by the occurrence of single and double peaked hydrograph responses, characterised by primarily new water (first peaks) and old water (second delayed peak) components (Wrede *et al.*, 2015). The occurrence of double peaks is generated by storage release processes, different from the rainfall-driven hydrographs, whose magnitude and timing reflected the rainfall distribution (Scaini *et al.*, 2017b).

### 6.3 MATERIALS AND METHODS

#### 6.3.1 Hydrometric monitoring

Natural precipitation was recorded by a tipping bucket rain gauge (Campbell Scientific Ltd., model 52203) located 3.5 Km from the experimental catchment, at the Roodt automatic weather station. Hydro-meteorological time series from the period November 2012 until December 2015 are available at 15-min time step.

Groundwater table depth fluctuations were monitored at 3 locations in the Weierbach catchment using OTT CTD sensors. Three 3-in diameter groundwater wells were drilled in 2009 and are located on the plateau (GW1), close to the stream channel (GW2) and at the bottom of the hillslope, 12 m from the stream (GW3) (Figure 29.b). During the period, groundwater table depth fluctuations were recorded at 15-min intervals in GW1, GW2 and GW3.
Changes in soil moisture and movements of the wetting front were estimated with 5 water content reflectometers (WCR – CS616, Campbell Scientific, Ltd.). Three sensors were installed horizontally at 10 cm depth, and two vertically between 50 and 80 cm depth. A multi-parameter WCR sensor (CS650, Campbell Scientfic Ltd.) was installed vertically at the middle of the plot at 50 to 80 cm depth. It recorded electrical conductivity (EC) and soil VWC at 15-min intervals.

Stream water level at the outlet (Q1) was measured using a pressure transducer (ISCO 4120 Flow Logger) in combination with a V-notch weir (Figure 29). Runoff at the outlet was continuously recorded at 15-min intervals.

![Figure 29. Map of the Weierbach catchment, in Luxembourg, showing the location of the discharge at the outlet (Q1), the 3 groundwater wells (GW1, GW2, GW3) and the soil moisture probes (SM) used in this study. The computed distance to the stream is shown for the hillslopes of the catchment (the correspondent colour ramp is shown in the legend). The plateau, defined as the areas having slope <6.5°, is indicated in grey.]

6.3.2 Electrical conductivity

Electrical conductivity (EC) was used as tracer to analyse the changes during rainfall events. Our assumptions are that (i) the change in EC is caused by water that
transports weathering products and (ii) during a rainfall event we can expect both increase or dilution process (more frequent in the alpine due to event rainfall, i.e. Rinderer et al. 2016). Other processes can alter EC but our assumption is that the change in EC is caused by new water diluting or transporting chemical tracer. EC data is used as it can be measured continuously or at short intervals resulting in time series that capture a large number of events.

Three different probes were used to monitor EC. The EC at the outlet (Q1) was continuously monitored using a conductivity probe (WTW 3310). The OTT CTD sensor in GW3 was also set to record EC and temperature data. Finally, the multi-parameter WCR sensor located at 65 cm depth (Scaini et al., 2017a) was used to infer EC data, used as an indication of tracer arrival (Dalton et al., 1984; Persson, 1997). All the probes were set to record at 15 min time step.

6.3.3 Rainfall events detection

A series of natural rainfall events was selected for the analysis. The selection criteria focused on rainfall events of a total of at least 2 mm. Each event was considered separate when the time elapsed from the previous event was at least 12 h. To focus on larger events, a second storm event definition was used: the threshold was identified with regard to rainfall size (15 mm) and elapsed time from the previous event (3 h).

Rainfall characteristics such as intensity, duration and average rate (total rainfall divided by total duration, expressed in mm h$^{-1}$), and the timing of stream and groundwater response were calculated for each rainfall event using the procedure shown in Rinderer et al. (2016). The selected events do not include delayed inflow from snowmelt, a marginal process in the area (Pfister et al., 2005), and do not detect both first and second peak in double-peak hydrographs, but only the highest in magnitude.
6.3.4 Analysis of measured data

6.3.4.1 Catchment wetness indicators

The data of Roodt automatic weather station were also employed to compute indicators of catchment wetness, in particular Antecedent Precipitation Index, API, calculated for 1, 7 and 30 days prior to each rainfall event. In order to have an indication of the antecedent moisture conditions (AMC) within the catchment, daily means of soil moisture were computed using 3 probes at 10 cm and 3 probes at 65 cm depth, as well as average soil temperature at daily aggregates.

Daily time step data of water balance and storage deficit were obtained following the method used in Pfister et al., (2017), where daily water balance was calculated over a period of 9 years (2006 to 2014) using data of precipitation, discharge at outlet of the Weierbach and potential evapotranspiration. From the maximum value of the water balance, the value of the maximum filled storage was estimated and used to compute daily changes in storage.

6.3.4.2 Timing metrics

For this analysis, three main metrics were used to characterise the timing of groundwater and streamflow response:

(i) lag to rise (as the elapsed time between the start of the rainfall event and the first response of the groundwater level or discharge),

(ii) lag to peak (the elapsed time between the start of the rainfall event and the groundwater or discharge peak) and

(iii) lag to recession - defined as the elapsed time when 20% of the total rise on the falling limb was reached.

The lag metrics were all calculated from the elapsed start of the rainfall event and used to calculate indices of the differential rise for each event – in particular:

(iv) start-peak lag, calculated as the difference between lag to peak and lag to rise, for all the groundwater wells and the discharge.
The implication of the use of these lags for celerity estimation are that (i) the lag to rise includes some integral distributed unsaturated zone celerities and downslope celerities; (ii) the lag to peak includes integral peak recharge travel times; (iii) and, in addition to the above, the lag to recession includes some integral of unsaturated celerity after rainfall peak and downslope celerity after recharge peak.

The values of groundwater level and discharge corresponding to lag to rise and lag to peak were also identified. For each event, the difference between water table peak and water table start was computed and used as groundwater range (GW range) for each groundwater well. Moreover, to analyse the reaction timings of groundwater, the difference between lag to rise relative to Q and lag to peak relative to Q was computed for each groundwater well.

The timing metrics were also identified for the EC data (Section 6.3.2). As the dynamic of EC could be variable, i.e. EC could be either diluted or increased during an event, both rise and decrease of EC data were recorded, and the corresponding magnitudes of EC variation were compared to each other in order to (i) remove unreliable data, when the EC signal was not clearly responding to the rainfall event, and (ii) use the corrected EC timing metrics. The large number of events analysed allowed to characterise the variability of the EC response, but also its average behaviour in terms of time to start of dilution.

### 6.3.4.3 Distance metrics

Distance metrics were used to calculate celerities for the lateral subsurface flow to the stream, and to the groundwater monitoring sites (except GW1 and GW6 on the plateau) and vertical celerities of the wetting front measured at 10 and 65 cm soil depth and at the depth of the water table.

1. **Distance to the stream**: used for calculating celerity of streamflow response (CQ) was defined as the average flow distance from each pixel on the hillslopes to the stream using a d8-flow algorithm.

2. **Distance to the groundwater well**: used for calculating celerity of lateral subsurface flow to a groundwater well (CW), was defined as the average flow
distance from all upslope contributing pixels to the groundwater monitoring location using a d8-flow algorithm.

3. Vertical distance to the groundwater table: The vertical distance was defined as the distance between the soil surface and the water table measured at the time of first response and time of peak of each rainfall event – i.e. two vertical distances per event. Vertical and lateral distances were computed for GW2 and GW3; for GW1, located on the plateau, only vertical distance was calculated.

4. Vertical distance to shallow and deep soil depth – the vertical distance was defined as the distance from the soil surface to the soil moisture probes at 10 and 65 cm depth. No lateral distance was defined for the soil moisture probes.

6.3.4.4 Celerity estimates

Initial and integral celerity responses were estimated using respectively (i) the initial response (time between rainfall start and start of soil moisture, discharge and groundwater table response) and (ii) the peak integral response (time between rainfall start and peak of soil moisture, discharge and groundwater table response). Depending on the site analysed, the celerities were considered as vertical or lateral propagation of the wetting.

It is generally assumed that water table gets deeper upslope, indicating that there can be no downslope contribution prior to the first water table rise at a site. Therefore, we use the initial groundwater response as a vertical celerity index (as supported by the work of Scaini et al., 2017a). For the integral celerities, though, the celerity will be a combination of integral vertical and integral downslope contributions and increasing with distance upslope as more of the slope gets recharged and sends an effect downslope.

The vertical celerities were calculated for (i) the initial and integral response of the soil moisture probes (as defined in Scaini et al., 2017a), (ii) the initial response of the wells on the hillslope and (iii) the initial and integral response of the well on the plateau.
Therefore, for each event, we calculated the following vertical celerity indices:

1. CSM10\text{rise}, CSM65\text{rise}, computed by dividing the soil moisture depth (10 and 65 cm respectively) to the lag to rise
2. CSM10\text{peak}, CSM65\text{peak}, computed by dividing the soil moisture depth (10 and 65 cm respectively) to the lag to peak
3. CW\text{rise}, computed by dividing the groundwater depth corresponding to the lag to rise, by the lag to rise – applied to GW1, GW2, and GW3;
4. CW1\text{peak}, computed by dividing the peak groundwater depth by the lag to peak – only for GW1 as previously explained.

For these sites we can assume that the first response following rainfall will be a good indication of the celerity of a wetting front in the unsaturated zone. In the case of GW1, we also expect the peak rise to be predominantly governed by vertical recharge.

Lateral celerities were calculated based on the work of Scaini et al. (2017b) for (i) the integral response of the wells GW2 and GW3 on the hillslope (CW\text{peak}), and (ii) the initial and integral response of the streamflow (CQ\text{rise} and CQ\text{peak}). In the case of the stream, the initial rise of streamflow will be a combination of the initial response in the riparian area and routing through the channel network. Streamflow peaks represent an integral of the hillslope runoff contribution including likely fast pathways through the bedrock fractures of hillslopes (Wrede et al., 2015; Jackisch et al., 2016; Martínez-Carreras et al., 2016). For the groundwater table response, applied to the wells located within the hillslope system (GW2 and GW3) the response will show the integrated vertical and lateral response over the saturated zone response upstream of the well. For the discharge, it represents an integral of the hillslope and channel network responses.

We calculate the following lateral celerity indices:

5. Initial event celerity, CQ\text{rise}, was estimated using the time between rainfall start and start of rise in streamflow discharge at the outlet, divided by the mean flow length to the catchment outlet;
6. Integral event hydrograph celerity, $C_{Q_{\text{peak}}}$, was estimated, using the time between rainfall start and peak discharge at the outlet divided by the mean flow length to the catchment outlet;

7. Integral hillslope celerity ($C_{W2_{\text{peak}}}$ and $C_{W3_{\text{peak}}}$) was estimated using the time frame between rainfall start and peak of groundwater table response of the wells GW2 and GW3, divided by the mean flow length to each well.

In the case of each well responses, the lateral distance information (Section 6.3.4.3) was divided by the lag to peak (to compute $C_{W_{\text{peak}}}$), both calculated from the start of the rainfall event (Section 6.3.3.2 and 6.3.3.3).

### 6.3.4.5 Velocity estimates

The velocity estimates were obtained using the EC information at three locations – GW3, SM65 and Q1 (Section 6.3.1 and 6.3.2). The velocity indices were estimated matching the corresponding celerity metrics, i.e. vertical for the soil moisture estimates, and for the initial velocity at GW3, and lateral for the integral hillslope velocity at GW3 and for the stream velocities. The following velocity indices were calculated:

1. $V_{\text{SM65}_{\text{rise}}}$, dividing the soil moisture depth (10 and 65 cm respectively) to the lag to rise of EC;
2. $V_{\text{SM65}_{\text{peak}}}$, dividing the soil moisture depth (10 and 65 cm respectively) to the lag to peak of EC;
3. $V_{\text{GW3}_{\text{rise}}}$, dividing the groundwater depth corresponding to the lag to rise, by the lag to rise of EC;
4. Integral hillslope velocity, $V_{\text{GW3}_{\text{peak}}}$, dividing the mean flow length to the well to the time frame between rainfall start and peak of EC of GW3;
5. Initial velocity, $V_{\text{Q}_{\text{rise}}}$, dividing the mean flow length to the catchment outlet to the time between rainfall start and start of rise of EC at the outlet;
6. Integral event hydrograph velocity, $V_{\text{Q}_{\text{peak}}}$, dividing the mean flow length to the catchment outlet by the time between rainfall start and peak EC.
The first event definition (2 mm and 12 h) did not generate events with clear EC dynamics due to the small size of events, therefore velocities were computed only for the 15 mm and 3 h events.

6.4 RESULTS

In order to quantify the coupling of response in the unsaturated and saturated zone and response in streamflow at the catchment outlet we calculated the Pearson’s correlation coefficients (r). Table 12 shows the relationship between time series, analysed as a first check for relationships between variables. The Pearson’s correlation coefficients (r) between the entire time series of discharge and the groundwater time series for GW1 and GW3 is greater than 0.7 and 0.58 for GW2. The groundwater time series GW1, GW2 and GW3 were also correlated with each other, namely GW1 and GW3 (r = 0.73), GW1 and GW2 (r = 0.53) and GW2 and GW3 (r = 0.54) despite being located on the plateau (GW1) and at the slope bottom (GW2 and GW3). Soil moisture time series were not correlated with streamflow nor with groundwater but soil moisture time series were correlated with each other (SM10 and SM65: r = 0.98).

Table 12. Correlation matrix for the time series (hourly data used). The Pearson’s correlation coefficient (r) between rainfall (P), discharge at outlet (Q1), each of the groundwater wells and the soil moisture probes at two depths (SM10 and SM65) are provided. Orange: r ≥ 0.5; Red: r ≥ 0.7. For the location of the wells see Figure 29.

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>Q</th>
<th>GW1</th>
<th>GW2</th>
<th>GW3</th>
<th>SM10</th>
<th>SM65</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q1</td>
<td>0.00</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GW1</td>
<td>0.00</td>
<td>0.71</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GW2</td>
<td>0.02</td>
<td>0.58</td>
<td>0.53</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GW3</td>
<td>0.03</td>
<td>0.75</td>
<td>0.73</td>
<td>0.54</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SM10</td>
<td>0.09</td>
<td>0.10</td>
<td>-0.19</td>
<td>0.02</td>
<td>-0.12</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>SM65</td>
<td>0.06</td>
<td>0.05</td>
<td>-0.16</td>
<td>0.03</td>
<td>-0.08</td>
<td>0.98</td>
<td>1.00</td>
</tr>
</tbody>
</table>
6.4.1 Rainfall event characteristics

Table 13 summarizes the characteristics of 198 rainfall events between November 2012 and December 2015 having cumulative rainfall greater than 2 mm (Section 6.4.2). In addition to the number of events with cumulative rainfall of more than 5, 10 and 15 mm, the minimum and maximum rainfall intensity and cumulative rainfall are given for each year analysed.

Table 13. The total number of events detected for each year, including the number of the events with cumulative rainfall of more than 5, 10 and 15 mm respectively are shown. Characteristics of the rainfall events in terms of minimum and maximum intensity (calculated over the full event duration) and cumulative rainfall are also shown. *Year 2012 not complete – data starting in 09/2012

<table>
<thead>
<tr>
<th>year</th>
<th>n events</th>
<th>&gt;5mm</th>
<th>&gt;10mm</th>
<th>&gt;15mm</th>
<th>min intensity</th>
<th>max intensity</th>
<th>min mm</th>
<th>max mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2012*</td>
<td>16</td>
<td>10</td>
<td>7</td>
<td>5</td>
<td>0.06</td>
<td>0.94</td>
<td>2.5</td>
<td>51</td>
</tr>
<tr>
<td>2013</td>
<td>58</td>
<td>39</td>
<td>27</td>
<td>14</td>
<td>0.09</td>
<td>5.69</td>
<td>2.2</td>
<td>45.9</td>
</tr>
<tr>
<td>2014</td>
<td>89</td>
<td>34</td>
<td>16</td>
<td>12</td>
<td>0.13</td>
<td>24.8</td>
<td>2</td>
<td>50.7</td>
</tr>
<tr>
<td>2015</td>
<td>55</td>
<td>28</td>
<td>15</td>
<td>11</td>
<td>0.1</td>
<td>4.4</td>
<td>2.1</td>
<td>71.4</td>
</tr>
<tr>
<td>total</td>
<td>198</td>
<td>111</td>
<td>84</td>
<td>42</td>
<td>0.06</td>
<td>24.8</td>
<td>2</td>
<td>71.4</td>
</tr>
</tbody>
</table>

A total of 96 summer events (March 21st - September 21st) were chosen out of the 198 total events, with total event rainfall of 11.3 ±11.2 mm (standard deviation), with a maximum of 71.4 mm, and duration of 21.5 ±22.0 h. In turn, winter events were 102 (16 of them in 2012), with total event rainfall of 10.8 ±11.5 mm (maximum of 51 mm) and duration of 28.9 ±22.8 h.

6.4.2 Response timing analysis

To analyse the response characteristics of soil moisture, groundwater tables and streamflow in the Weierbach catchment, the lag to rise and lag to peak were calculated for the 198 events comprised in the broader rainfall event definition (2 mm and 12 h).
6.4.2.1 Lag to rise and lag to peak

Table 14 shows the information on each well and on the discharge at outlet, including the number of events with a response (from the total of 198 rainfall events analysed). As the monitoring was not permanent during the studied period, each well had a different number of rainfall events. Out of the 198 rainfall events, 197 produced a rise in discharge, with lag times between 15 and 3585 minutes. The lag time between rainfall and discharge peak ranged between 30 and 6615 min – with a total of 137 events producing a distinctive peak (Table 14). The lag between rainfall and groundwater table response ranged between 15 and 7170 min (GW1), 15 and 3735 min (GW2), and 15 and 3945 min (GW3). The lag between rainfall and groundwater table peak ranged between 120 and 4425 min (GW1), 135 and 7020 min (GW2), and 60 and 7200 min (GW3).

Table 14. Statistics for the data of the rainfall events per each site. The % of missing data, number of events with data, and of those events the ones where an observed rise and peak respectively was observed are shown. Further, the minimum and maximum lag to start and lag to peak are also shown.

<table>
<thead>
<tr>
<th>Site</th>
<th>Missing data</th>
<th>events with data</th>
<th>events with response</th>
<th>events with peak</th>
<th>Min lag to start</th>
<th>Max lag to start</th>
<th>min lag to peak</th>
<th>max lag to peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>GW1</td>
<td>2.2</td>
<td>178</td>
<td>110</td>
<td>76</td>
<td>15</td>
<td>4425</td>
<td>120</td>
<td>7125</td>
</tr>
<tr>
<td>GW2</td>
<td>22.0</td>
<td>164</td>
<td>108</td>
<td>71</td>
<td>15</td>
<td>3735</td>
<td>135</td>
<td>7020</td>
</tr>
<tr>
<td>GW3</td>
<td>15.9</td>
<td>172</td>
<td>132</td>
<td>84</td>
<td>15</td>
<td>3945</td>
<td>60</td>
<td>7200</td>
</tr>
<tr>
<td>Q</td>
<td>0</td>
<td>197</td>
<td>197</td>
<td>137</td>
<td>15</td>
<td>3585</td>
<td>30</td>
<td>6615</td>
</tr>
</tbody>
</table>

The box plots in Figure 30 show the difference between lag to rise (left) and lag to peak (right) of groundwater levels relative to streamflow (Section 6.3.4.2): the median values were 105, 90 and 45 min in respectively for GW1, GW2 and GW3, indicating an overall faster response in the well located at the bottom of the hillslope, GW3, as the median lag to rise of GW3 is half that of the others. The median values for lag to peak were 705, 645 and 165 min (GW1, GW2 and GW3, respectively). In both lag to rise and lag to peak data, GW3 had a smaller interquartile range then the others which indicates less variability with respect to discharge in initial and integral response timing for the well in foot slope location than for the well in mid and upslope location for the majority of the events. In the majority of the events, streamflow responded prior to the groundwater levels.
(positive lag times), but with a very large range of possible responses. In turn, only in few cases the peak occurred in the wells before than in the streamflow –respectively 12, 4 and 10 events.

![Box plots showing the difference between lag to rise (left) and lag to peak (right) of groundwater levels relative to streamflow– calculated for each rainfall event. Positive values indicate discharge response preceding groundwater response, while negative values indicate that streamflow response lags groundwater response. The % of events during which groundwater or streamflow responded first, is shown below the well name on the x axis. (On each box, the central red mark is the median, the edges of the box are the 25th and 75th percentiles, whilst the black whiskers show the 5th and 95th percentiles. Red crosses indicate events with >3 standard deviations).](image)

**6.4.2.2 Lag to recession**

The time to recession metric (Section 6.3.3.3) was also calculated to provide information on the dynamics between groundwater and hydrograph recession. Figure 31 shows the difference in time to recession of groundwater levels relative to streamflow for all rainfall events. The number of events for which differences in lag to recession of groundwater relative to streamflow could be determined was smaller than the number of events used for the difference in lag to rise and lag to peak of groundwater relative to streamflow, as groundwater levels often did not decrease to full recession because a consecutive rainfall event caused groundwater levels to increase again. Median differences in lag to recession in streamflow was shorter than median differences in lag to recession of groundwater levels in GW (180, 105 and 90
minutes respectively for GW1, GW2 and GW3). However, for more than 13 events the lag to recession in streamflow was longer than lag to recession in groundwater levels (17 events for GW3, Figure 31). Also in the case of lag to recession, the well located at the bottom of the slope, GW3, had a much smaller interquartile range, indicating less variability between groundwater and streamflow dynamic.

Figure 31. Box plots showing the difference in lag to recession in groundwater levels relative to streamflow calculated for all rainfall events. Positive values indicate that lag to groundwater recession is longer than lag to streamflow recession, while negative values indicate the opposite case. The % of events during which groundwater recession or streamflow recession was shorter is shown below the well name on the x axis.

6.4.2.3 Controls on catchment streamflow response to rainfall events

Figure 32 shows the relationship between groundwater and streamflow start-peak lag (Section 6.3.3.2). All the groundwater wells are related to the discharge dynamic in that the start-peak lag increases with the increase of streamflow’s start-peak lag, but the relationship is scattered. The two event definitions (2 mm and 12 h vs 15 mm and 3 h) are indicated by empty circles and filled diamonds respectively.
Figure 32. Relationship between the streamflow start-peak lag (a measure of the rising limb), and the groundwater start-peak lag, for GW1 (a), GW2 (b) and GW3 (c) respectively. The figure shows the events of the 2 mm and 12 h (circles) and those of 15 mm and 3 h (diamonds).

Figure 33 shows the relationship between the lag to rise and rainfall duration (a), total rainfall (b), storage deficit (c), API1 (d), API7 (e) and API30 (f). Each metric is plotted against lag to rise of GW1, GW2, GW3 and streamflow at the outlet. Wetness indicators were poorly related to the lag of rise of both groundwater levels and streamflow (Figure 33).
6.4.3 Celerity and velocity estimates

6.4.3.1 Vertical and lateral celerities

Estimates of the celerity indices for both lateral and vertical responses, as presented in Section 6.3.3.3, are shown in Figure 34. Median groundwater vertical celerities were equal to 0.36 m h\(^{-1}\) (GW1\(_{\text{rise}}\)), 0.26 m h\(^{-1}\) (GW2\(_{\text{rise}}\)) and 0.86 m h\(^{-1}\)

Figure 33. Analysis of explanatory variables that could influence the lag to rise of groundwater and streamflow. The scatter plots show the relationship between the start lag and the rainfall duration (a), total rainfall (b), storage deficit (c), and for each metric the 4 scatterplots refer to GW1 (upper left), GW2 (upper right), GW3 (bottom left) and discharge at outlet (bottom right).
(CW3\textsubscript{rise}), and the median soil moisture celerities were equal to 0.05 and 0.52 m h\textsuperscript{-1} (CSM10\textsubscript{rise} and CSM65\textsubscript{rise} respectively) (Figure 34.a). The peak vertical celerities were computed for the well located on the plateau, resulting in a median value of 0.03 m h\textsuperscript{-1} (CW1\textsubscript{peak}), and for the soil moisture, with medians of 0.01 m h\textsuperscript{-1} (CSM10\textsubscript{peak}) and 0.08 m h\textsuperscript{-1} (CSM65\textsubscript{peak}) respectively (Figure 34.b).

![Figure 34](image.png)

Figure 34. Box plot of each vertical celerity index estimated using groundwater response timings of each well and soil moisture. Peak vertical celerity was computed for CW1\textsubscript{peak} and the soil moisture only (Section 6.4.3). Celerity values larger than 3 standard deviations are indicated by red crosses.

![Figure 35](image.png)

Figure 35. Box plot of lateral celerity indices estimated for discharge – both CQ\textsubscript{rise} and CQ\textsubscript{peak} – and peak groundwater table response, respectively CW2\textsubscript{peak} and GW3\textsubscript{peak}. Celerity values larger than 3 standard deviations are indicated by red crosses.
Overall, the lateral celerity indices were orders of magnitude larger than vertical. The median $CQ_{\text{rise}}$ was 100.0 m h$^{-1}$ (Figure 35.a) and the median $CW_{\text{peak}}$, $CW_{\text{3peak}}$ and $CQ_{\text{peak}}$, were 2.2, 1.0 and 7.9 m h$^{-1}$ respectively (Figure 35.b). The very high celerities estimated for $CQ_{\text{rise}}$, larger than the integral metric, are linked to the fact that in the majority of the events the streamflow responded within less than one hour (and many within the first 15 minutes).

6.4.3.2 Controls on celerity response to rainfall events

For the present analysis we are using the event definition of 15 mm and 3 h, as the data were not meaningful for the lower event definition (2 mm and 12 h).

Figure 36 shows the relationship between rainfall rate (total event rainfall divided by total event duration) and rise celerities, for the three wells ($CW_{\text{1rise}}$, $CW_{\text{2rise}}$ and $CW_{\text{3rise}}$) and the discharge ($CQ_{\text{rise}}$). The relationships do not show a clear relation between the rise indices and rainfall rate, especially in the cases of GW3 and Q1 where a large number of rainfall rates corresponded to the highest celerities (Figure 36.c, 36.d).

Figure 36. Scatterplots of rainfall rate expressed as total mm divided by total time of the event, plotted against the four types of $C_{r}$: $CW_{\text{1rise}}$ (a), $CW_{\text{2rise}}$ (b), $GW_{\text{3rise}}$ (c) and $CQ_{\text{rise}}$ (d). Only the events >15 mm are shown.
Figure 37 shows the relationship between the rainfall rate (total event rainfall divided by total event duration) and the peak celerities, both vertical (CW1\textsubscript{peak}) and lateral (CW2\textsubscript{peak}, GW3\textsubscript{peak} and CQ\textsubscript{peak}). In general celerities are linearly related to rainfall rate, with a good correspondence between integral celerities and rainfall rate. However, a high variability is observed at low celerity-intensity rate, while a low number of high celerities corresponded to the highest rainfall rates.

![Figure 37](image)

**Figure 37.** Scatterplots of rainfall rate expressed as total mm divided by total time of the event, plotted against the four types of C\textsubscript{s}: CW1\textsubscript{peak} (a), CW2\textsubscript{peak} (b), GW3\textsubscript{peak} (c) and CQ\textsubscript{peak} (d). Only the events >15 mm are shown.

### 6.4.3.3 Velocity/celerity relationship

Velocity responses estimated monitoring EC from a soil moisture probe, in a groundwater well and at the catchment outlet (Section 6.3.4.5), were compared to the corresponding celerity estimates. Figure 38 shows the relationship between rise celerities and rise velocities (squares), and peak celerities and peak velocities (circles), for GW3, streamflow at outlet and SM at 65 cm depth. The unsaturated indices do not relate to each other, and the saturated indices are not much related. Only the saturated discharge celerity and velocity show a close-to linear relationship (Figure 38.b).
6.5 DISCUSSION

6.5.1 Celerities and effective distance estimates

The framework proposed in this work provided preliminary results regarding the use of easily available in situ data to estimate and compare velocities and celerities. Our results showed a lack of strong relationships between celerity and antecedent wetness conditions (Figure 36 and 37), and an overall weak relationship between celerity and velocity. This could be due to poor approximations of velocity, or related to the distance metrics chosen to define celerity.

The lateral $C_{\text{rise}}$ were one order of magnitude higher than lateral $C_{\text{peak}}$, possibly due to the effective distance used to compute $C_{\text{rise}}$, which is smaller than the
effective distance integrating the celerity responses for the peak. On the contrary, the range of lateral celerities estimated from discharge data (CQ\textsubscript{rise}), show much higher values than the data of Scaini et al. (2017b). The distance relative to the CQ\textsubscript{rise} used in the present study was computed using the mean Euclidean distance to the stream instead than the mean riparian zone distance, which was the metric used in the work of Scaini et al. (2017b).

Lateral celerities are faster than vertical celerities, therefore, the storage deficit filled in the water table rise must be small. If the initial response is much faster than the integral (peak celerity) response, that means that the effective storage filled in the unsaturated zone in order to reach initial wetting is much greater than the effective storage necessary to reach the peak, suggesting a much smaller pore volume involved. This invokes the occurrence of preferential flow processes. Another possibility is that effective distances used to quantify lateral celerities were overestimated, leading to larger celerities than reality. In particular, if effective upslope distance is less under dry conditions than under wet, then celerity would appear larger than it really is using a fixed distance definition (see Barling et al., 1994).

Our framework to select metrics to compare velocities and celerities was linked to choosing the distance information based on the perceptual functioning of the catchment, following recent research (Wrede et al., 2015; Martínez-Carreras et al., 2016). The groundwater wells located towards the bottom of the slopes, GW2 and GW3, rarely responded before the stream, contrarily to the idea of the hillslopes contributing to the first stream response, and meaning that the distances used to compute velocity and celerity indices might have been required to be chosen differently. The distance metrics chosen, despite being supported by recent literature (Section 6.5.3), once put in practice show that there is a lack of groundwater contribution to stream rise, suggesting distances are overestimated, as well as the very high lateral celerities (Figure 35).
6.5.2 How are groundwater and discharge response times related to wetness indicators?

The response, timing, and dynamic range of discharge and groundwater response was analysed for 198 events occurring between November 2012 and December 2015 from rainfall events of a total of at least 2 mm and separated by at least 12 h (Section 6.3.3). In the majority of the cases, the initial rise in outlet discharge of the Weierbach catchment preceded the initial rise in the groundwater wells, with median values equal to 105, 90 and 45 min for GW1, GW2 and GW3 (Figure 30). This behaviour was previously observed in the work of Martínez-Carreras et al., (2016) who found a lack of groundwater contribution to the initial rise in stream discharge. The lag to peak had an even more pronounced difference between the discharge and groundwater peaks, with a median delay of 705, 645 and 165 min for GW1, GW2 and GW3, respectively (Figure 30). GW3 rise and peak coincided more closely to the discharge, while GW1 and GW2 are delayed relative to the discharge peak. This suggests that the upper slopes of the catchment (represented by GW1 and GW2) have a stronger role in providing the discharge recession curve relative to GW3. In some cases, groundwater responded before the discharge (Figure 30). In the majority of those cases, the 3 wells were responding 15 to 45 minutes before, or concomitantly, with discharge.

The difference between the lag to rise and lag to peak in the GW and streamflow responses is also most likely due to the contribution of the channel and riparian areas to the hydrograph which is not well represented by any of the available well observations. In a study performed on 18 piezometers in a 220 m$^2$ study site in Canada, a gradient of response was observed, with piezometers close to the stream responding before streamflow and opposite behaviour (and lower correspondence to stream dynamics) observed for piezometers located more than 8 m uphill (Haught and Van Meerveld, 2011). GW3 seems to be closer to this type of response, but is at a similar distance from the stream and similar groundwater depths to GW2 which shows a more delayed response. Other studies used water table responses as an index of connectivity (i.e. water table continuity between upland and stream elements of the catchment) for hillslope segments (Smith et al., 2013) and found that
streamflow generation could be predicted by a model based on the topographic form. The three studied wells are also in the forested part of the catchment, whereas the riparian area tends to be less covered. Interception by the canopy might amount to 15-50% of rainfalls, especially for the broadleaf trees (Gerrits et al., 2010), and could contribute to a faster stream response relative to groundwater rise.

Overall, the response of GW3, located at the bottom of a convex hillslope, was similar to the discharge, as shown by the low interquartile range of the box plot and the high correlation coefficient between discharge and GW3 (0.73) observed for the full series (Table 12) even if the relationship between start-peak metrics relative to discharge was scattered for all the wells (Figure 32). The rise of the groundwater table at the hillslope base at the same time as – and sometimes before – discharge increase is a common perception of hillslope groundwater contribution (Mosley, 1979; Sklash and Farvolden, 1979; Kim et al., 2004; McGuire and McDonnell, 2010). The work of Jencso et al. (2009, 2010) found that the timing and duration of groundwater connectivity between hillslope and riparian zones was acting as a first-order control on the magnitude and timing of water and solutes observed at the catchment outlet. However, in the majority of the 198 events observed here, the stream response preceded that of groundwater (as observed in other studies, i.e. Weyman, 1970; Harr, 1977; Turton et al., 1992; Montgomery et al., 1997; Camporese et al., 2014; Penna et al., 2015). In particular, GW3 responded after the stream in 75% of the events, and in 86% of the events, GW3 peaked after the stream (Figure 30). This suggests that, at least for those events, groundwater and hillslope connectivity did not contribute to the initial streamflow rise though are likely controlling the shape of the discharge recession and potentially contributes to the double peak phenomenon observed by others (Wrede et al., 2015; Martínez-Carreras et al., 2016), though multi-peaked events were not specifically studied here.

The groundwater response in relation to discharge was poorly related to the explanatory variables we have explored (API, AMC, rainfall characteristics and storage deficit, Section 6.4.2.3). It appears that soil moisture and antecedent wetness conditions largely do not affect the time it takes for rainfall to make groundwater rise (Figure 33), in contrast to other studies who found that lag times
decreased with increasing moisture (Turton et al., 1992; Haught and Van Meerveld, 2011). We expected – but did not find – a relationship between shorter lag times and wetter antecedent conditions or larger intensity events (Figure 33). This suggests that some kind of static control, unrelated to wetness conditions, could cause the delay between groundwater and streamflow. In particular, the response might be related to the distinctive 2-layered structure suggested in (Scaini et al., 2017b), with a prevalent vertical flow direction in the soil layer and lateral flow direction in the fractured bedrock. Here, the few occasions where hillslopes peak before the streamflow would then reflect that such a lateral flow direction would be activated only on certain conditions, when the hillslopes contribute to the hydrograph response. Such conditions could be linked to a fill-and-spill type of response, as observed in the work of (Tromp-van Meerveld and McDonnell, 2006), and complex controls on their connectivity could contribute to the poor relationships observed here between the hillslope groundwater response and traditional antecedent wetness indicators.

6.5.3 How are vertical and lateral celerities related across the catchment?

Estimating celerities from groundwater and discharge data allows for a comparison that goes beyond the lag and response time analysis as it accounts for distance information. We apply a methodology first described in Scaini et al. (2017b) and expand its application to wells located on different parts of the catchment in order to estimate celerities.

In order to be consistent with known properties at each site, we estimated vertical celerities, for the first water table response at each well and using soil moisture information at 10 and 65-cm depths (as in Scaini et al., 2017a), and lateral celerities using the peak information in the wells located in the hillslopes and from discharge response. The vertical celerities correspond to the vertical wetting front movement through the soil, while the lateral celerities measure the hillslope and catchment response.

Analysing vertical celerity responses does not allow to discriminate between preferential flow or a more general wetting front, but allows for an analysis of the
limiting time for any water table response as it represents the first recharge. The permeable soils of the Weierbach catchment allow for high infiltration rates which are responsible for the a very fast wetting front response (Scaini et al., 2017a). The range of vertical celerities is similar to those observed in other studies on same soil types (Angermann et al. 2016; Scaini et al., 2017a) and other steep forested study sites (van Verseveld et al., 2017).

The groundwater response is linked to upslope and vertical infiltration inputs but we did not see a rise in groundwater prior to the rise of the discharge in the majority of cases (Section 6.4.2.1). Even GW3, which is highly coupled with the discharge dynamic (Figure 30, Table 12), only reacts before discharge in 25% of the cases and only peaks before discharge 14% of the time. This shows that discharge response does not always get a contribution from the pressure wave that propagates through the hillslopes, as the lateral celerities for the discharge are higher than those for the hillslope. However, our wells, located in the hillslope, did not capture the subsurface responses in the riparian area where water table is close to or at the surface – and likely responded more quickly to the rainfall inputs. In the same way, in the overall behaviour of the events analysed, we cannot see a strong contribution to the peak coming from the groundwater body. The option of the hillslopes contributing to the first (driven by rainfall) hydrograph peaks in this catchment as conceived by previous work (Jackisch et al., 2016; Martínez-Carreras et al., 2016), does not seem to hold, except perhaps in some riparian area where the water table will be closest to the surface.

The CW3_peak data showed a lower value range to the data of 21 rainfall events of more than 15 mm analysed in Scaini et al. (2017b), and the highest celerities were not only observed during summer events or where the intensity rate was the highest as for the data explored in Scaini et al. (2017b), where an influence of both event intensity and residual storage (summer, warm conditions) on celerity responses was suggested. The overall relationship between celerities and intensity rate observed in Scaini et al. (2017b) was confirmed in this study as the integral celerities show a linear relationship with the intensity rate, stronger for the peak celerities than for the
rise celerities (Figure 36 and 37). Instead, we did not observe a clear relationship with any of the wetness indicators used (data not shown).

The integral event hydrograph celerity index ($CQ_{\text{peak}}$) defined earlier, has some overlap with concepts from traditional unit hydrograph theory in hydrology of lag time and time of concentration. Lag time is often defined as the time from the centroid of effective rainfall to the peak of the hydrograph; time of concentration as the time taken from the end of the duration of effective rainfall for water to flow from the furthest point of the catchment to the outlet (e.g. USDA 2010). While these concepts can apply to both surface and subsurface flows, the idea of a time of concentration has been primarily linked to responses dominated by surface runoff, with velocities estimated from surface roughness coefficients. However, since we are interested primarily in the timing of the hydrograph response, lag time and time of concentration should be defined more properly in terms of celerities rather than water flow velocities, especially when it is primarily subsurface processes contributing to the hydrograph, as in the Weierbach. Even for surface runoff, however, we expect celerities to be faster than flow velocities (e.g. Beven, 2012), and we also know that surface runoff does not necessarily flow directly to the catchment outlet but can infiltrate and displace stored water (Imeson et al., 1992; Abdulkabir et al., 1996; Iorgulescu et al., 2005). Consequently, it might be appropriate to revisit these concepts based on celerities rather than velocities.

### 6.5.4 How do in situ velocities and celerities relate to each other?

A linear relationship was observed for the streamflow peak celerity, $CQ_{\text{peak}}$, and the corresponding velocity, $VQ_{\text{peak}}$ (Figure 38.e). Such a relationship is largely driven by high celerities with large velocities, however many of the events are characterised by small celerities and small velocities. It is likely that the velocity and celerity did not exhibit simple linear relationships in other compartments, represented in our analysis by GW3 and SM velocity information, as they are more complex and potentially controlled by different processes that occur at different time scales (Figure 38). Figure 38 also contains a few events where velocity is higher than celerity, particularly at low celerities. This tends to correspond to relatively dry conditions, when EC response may be reflecting only inputs from the riparian area.
An influence of tracer experiments on the EC dynamic of GW3 was observed: the rainfall events following Experiment 1 (Scaini et al., 2017a) generated a rise in EC, and concurrently the events analysed did not show a dilution effect. Also the EC derived from the TDR probe, in turn, rises during an event (no dilution observable). On the contrary, the stream EC data are characterised by low EC peaks, indicating dilution due to the rainfall falling on the stream channel rather than mobilization of stored, high EC water, to the stream channel.

6.5.5 Issues related to estimating celerities and velocities from in situ data

The time step used in the present work, 15 minutes, is widely used for streamflow monitoring, as it is considered to match the evolution of the hydrograph in headwater catchments (few hours). For the purpose of celerity-velocity analysis, though, it would be beneficial to have a higher resolution of the data, particularly at the beginning of the event, to improve the estimate of time to rise information, and therefore $CQ_{\text{rise}}$. In order to estimate celerities we require a better temporal resolution than 15 minutes. For example, one third of the storm events of more than 15 mm responded within the first 15 minute time step. Therefore, the increase in discharge could have occurred anytime between 0 and 15 minutes. Assuming 1 minute, the corresponding celerity for the initial rise would be equal to 4500 m h$^{-1}$; assuming 15 minutes, the first reliable discharge estimate, celerity to initial rise would be equal to 300 m h$^{-1}$, more than ten-fold difference. Despite the possibility of using integrated values, the variability and meaning of such a strong simplification would have an high effect on the relationship between celerities and antecedent conditions, as well as velocities.

Also in the case of the soil moisture, the 10 cm and 65 cm deep probes respond basically at the same time step – this issue was already discussed in the work of (Scaini et al., 2017a), where artificial rainfall intensities were very high. This study shows the same under natural conditions, as shown in Figure 34 where the 10 cm depth probes have unrealistic values compared to the 65 cm depth probes, and it is supported by the very high correlation between the probes (Table 12). A smaller time step would be required to compare in a meaningful way the celerity estimates derived from soil moisture.
Estimates of velocity with EC might not be appropriate, as its fluctuations are a consequence of many geochemical and transport processes rather than an actively introduced tracer. In our case, EC data used to compute velocity were often not reliable, because of an unclear EC signal reaction to the event. The use of the 15 mm events improved the EC response signal. Based on the large number of events analysed, the variability but also the average behaviour in terms of time to start of dilution can be better characterized. Other tracers can be near “ideal” in case of very low (or absent) natural abundance and conservative characteristics (Flury and Papritz, 1993; Nickus, 2001). In particular, water isotopes, and in particular high frequency stable isotopes, might in the future solve this time-step issue, even though at the present time the resolution is still too coarse, with a maximum time resolution of 30-min (Von Freyberg et al., 2017). A resolution of the velocity/celerity relationship remains an open question and one that may be approached using multiple catchment investigations and improved velocity estimates (from high-resolution tracer sampling and/or artificial tracers).

6.6 CONCLUSIONS

This study analysed the streamflow and groundwater response to natural rainfall events over a 4-year period in the Weierbach catchment (Luxembourg). We propose a framework for estimating both vertical and lateral celerities, at hillslope and catchment scales. Our main research questions were (i) How are groundwater and discharge response times related to wetness indicators? (ii) How are vertical and lateral celerities related across the catchment? (iii) How do in situ velocities and celerities relate to each other?

In response to these questions we found that:

(i) In response to a rainfall event, discharge tends to react very quickly, and in the 70% of the cases earlier than groundwater. We observed a lack of effect of the metrics of rainfall antecedent conditions and rainfall characteristics (e.g. duration, volume). The absence of relationship between lag to start and wetter antecedent conditions or larger intensity events, suggests that some static control, related to the characteristics of
the site, are controlling this delay. We also inferred the importance of the riparian zone in the response of the stream flow: the riparian zone must be reacting more quickly than the wells located at the bottom of the slopes, GW2 and GW3.

(ii) Celerity information can be estimated by using lag to rise, as well as lag to peak, both for groundwater, soil moisture and discharge data. Such information is useful in understanding complex interactions between groundwater and discharge response during natural rainfall events.

(iii) The relationship between velocity and celerity using the indices hereby presented showed an overall weak relationship between celerity and velocity. This could be due to poor approximations of velocity, related to the distance metrics chosen to define velocity and celerity, or due to the complexity of the velocity/celerity relationship.

In this catchment, the rapid response to rainfall occurs in the stream before it occurs in the groundwater. This suggests that groundwater and hillslopes contribute to the recession of the hydrograph, and initiation and peak is driven by rain falling in near-stream areas or moving by preferential flow to the stream channel. Celerity and velocity only appear to be correlated for the integral responses, i.e. the peak response, which could be due to how the celerities were defined or how the velocities were estimated.

A major focus of this work was to understand the role played by rainfall event characteristics on groundwater and streamflow response, determined using lag times as well as celerity estimates. We found that small rainfall contributions could induce rapid lateral flow even without generating a high rise in the water table. This suggests that a small pore volume, and likely preferential flow, is sufficient to generate a subsurface response. In catchments dominated by subsurface contributions to the hydrograph, as in the Weierbach catchment, lag time and time to peak should be defined in terms of celerities rather than water flow velocities.
7 CONCLUSIONS

“In the attempt to make scientific discoveries, every problem is an opportunity, and the more difficult the problem, the greater will be the importance of its solution”

Edward O. Wilson

Understanding the complex interactions between water storage and release in catchment and tracer transport processes allows for the resolution of the ‘old-water paradox’: where water stored within the catchment for months and years can be released in minutes and hours during a rainfall event. That resolution depends on the difference between the velocities and celerities in the catchment. The work in this thesis combined experimental and modeling approaches to better understand flow processes in steep, forested catchments. Artificial rainfall experiments were employed to provide tracer transport data as well as flow measurements. A particle-tracking model, the Multiple Interacting Pathways (MIPS), was set-up using data from the experimental manipulations and employed in a hypothesis testing framework.

Demonstrating the utility and application of velocity and celerity is important for the non-modeling community. The importance of the relationship between velocities and celerities is confounded by the difficulty in parameterising both velocities and celerities simultaneously across temporal and spatial scales. This thesis addressed one of the main challenges in modern hydrology, the integration, in a simple way, of measures of velocity and celerity into hydrological data analysis and modeling frameworks.

A main contribution of this work regards the response times and how to determine them in terms of velocity and celerity across different spatial scales, characterising the soil and bedrock structure and their changes through time. Figure 39 shows a comprehensive schema of the chapters 3, 4, 5 and 6 in light of the different scales and metrics studied.
Figure 39. (a) Sketch of the different spatial scales analysed in the present work with the corresponding chapter. (b) Enlarged sketch showing for each chapter the main flow processes analysed and including the velocity and celerity metrics employed, the main result, and the evaluation of the velocity/celerity metrics used.
Different techniques to measure wetting front and tracer movement through the soil were tested, showing that their comparison helps to gain information on the processes involved in runoff generation. In order to do this, different spatial scales were explored, using column experiments (Chapter 5), plot experiments (Chapter 3), hillslope scale (Chapter 4) and sub-catchment scale analyses (Chapter 6), to explore the simplest way to estimate and compare velocities and celerities, discussing how we can use their estimates to evaluate hypotheses on flow processes applied to the Weierbach catchment (Figure 39).

In Chapter 2, measures of velocity and celerity were defined, as well as their estimation using experimental approaches. Modelling strategies adopted so far in hydrology to characterise both velocities and celerities were also discussed.

In Chapter 3, velocities and celerities were assessed using geophysical and tracer techniques and it was shown that ERT-based MICS is able to capture infiltration patterns at plot scale. Vertical infiltration was observed to be the dominant process until 2-3 m depth, but the occurrence of preferential flow pathways was significant.

In Chapter 4, tracer transport from plot to stream was analysed at the hillslope scale. Rainfall and storage-driven discharge peaks were controlled by different mechanisms. Rainfall rate and residual storage control celerity responses. The orientation of cleavage fractures within the bedrock was shown to control flow direction, showing its importance in the prediction of fractures contribution to runoff.

Chapter 5 characterised the processes involved into the infiltration of water through an undisturbed column experiment coupled with a 1-D MIPs model. Different velocity distributions and transition probabilities matrices were explored showing the need to include an appropriate parameterisation that accounts for changes in the mobile water storage in time. The increase in the ability of MIPs to reproduce the flow and transport with the inclusion of transition probability matrices to include exchange between velocities in the whole profile was required to reproduce the infiltration in the soil of the Weierbach. The column model might help inform a hillslope or catchment version of MIPs.
In Chapter 6, the relationship between catchment-scale storage and discharge dynamics was explored. It was shown that by using simple metrics it is possible to effectively estimate the celerity response. There is a difficulty in choosing the appropriate distance scale for the celerity indices, depending on the hypothesised processes involved. It was also demonstrated that celerity indices provide an added value to classical analysis as lag times or hydrograph characterisation, in catchments dominated by complex subsurface runoff dynamics, where the traditional times of concentration should in fact be based on celerities, and not velocities.

In general, this work has shown that by using simple metrics it is possible to effectively estimate and compare velocity and celerity response across different scales. The conceptual process understanding originating from our study can be generalized to similar locations. In addition, this study showed the value of various modern experimental techniques to infer dominant processes.

**7.1 LESSONS LEARNED ABOUT THE WEIERBACH CATCHMENT**

The Weierbach catchment is an intriguing platform to explore the old-water paradox. In the introduction, we outlined the main unexplored questions regarding controls on the flow response dynamics: (i) the characteristics of the lower boundary, including the role of the fractured bedrock; (ii) the processes involved in the double peak response in the Weierbach catchment, and (iii) the main runoff generation mechanisms involved. Our work addressed these questions and informed on how the catchment works.

It was found that the flow through the soil was primarily vertical at least up to 3-4 m, and that the highly permeable material, on which the soil is developing, is responsible for the strong prevalent vertical direction of flow through the subsurface. In turn, the subsurface topography likely controls lateral flow generation. It was observed that a small pore volume needs to be filled in order to generate saturated conditions (Chapter 3). Corroborating this, at the different scales analysed, it was found that small rainfall amounts could induce rapid lateral flow even without generating a high rise in the water table. This suggests that a small pore volume is sufficient to generate a subsurface response. The high variability between maximum
velocities of different tracers indicated a complex pattern of tracer movement through the soil, not captured by celerity values alone. Our study demonstrated the importance to assess both velocities and celerities to understand flow dynamics in response to sprinkling while information on the wetting front alone would have missed important preferential flow processes.

Our results indicate that the single or first peak of double-peak events is rainfall-driven (controlled by rainfall) while the second peak is storage-driven (controlled by storage). The comparison between velocity and celerity estimates suggests a fast flowpath component connecting the hillslope to the stream, but velocity information was too scarce to support such a hypothesis (Chapter 4). Using soil moisture, well and discharge responses to infer celerity and electrical conductivity to infer velocity responses (Chapter 6) it was found that the velocity/celerity relationship is linear, but often overestimated because of distance measures used, with the exception of maximum celerities likely being underestimated due to the temporal resolution of the used probes.

The analysis of tracer movement at the hillslope scale demonstrates that subsurface flowpaths at the studied hillslope do not appear to align with the slope gradient. In contrast, they appear to follow the strike of the bedrock cleavage. These results have expanded our understanding of the importance of the subsurface, in particular the underlying bedrock systems, demonstrating the importance of cleavage orientation in controlling subsurface flow direction. This work further demonstrated the importance of quantifying the extent of fractures as well as their orientation relative to dominant topographically-related flowpaths.

The soil micro-structure of the horizons Ah and Bw was also studied in a hillslope of the Weierbach and confirmed the need for an immobile storage in order to reproduce the vertical movement of water through the soil. In fact, the immobile water hypothesis, coupled with a variable field capacity parameter, was the best-fit for modelling the column experiment in Chapter 5. This suggested that some portion of immobile water, as well as modification to the soil structure – represented in the model by a change in the field capacity parameter- were necessary to explain the observed solute and flow transport dynamics.
The storage-discharge analysis performed in Chapter 6 allowed to apply a framework of celerity and velocity estimation to the response times of three groundwater wells in relation to streamwater during rainfall events. We could conclude that both the first streamflow rise response and the development of streamflow peaks must be due to rain falling on the near-stream zone, at least in the 70% of storms where the stream responded before the hillslope, and 80% were discharge peaked before the hillslopes, contrarily to the idea of the hillslopes contributing to the first stream response. Concurrently, the distance metrics chosen, once put in practice show that there is a lack of groundwater contribution to stream rise, suggesting distances are overestimated, as well as the very high lateral celerities. Therefore, the streamflow mostly responds to rainfall events prior to the wells at the hillslope bottoms. Moreover, the first response timing of the streamwater is not primarily related to antecedent conditions, showing that the hillslope does not contribute to the hydrograph response during most of rainfall peaks as previous analysis suggested.

7.2 FUTURE WORK

Our study shows promising possibilities for the inclusion of celerity and velocity estimates in data analysis. The adaptability characteristics of the MIPs framework will be used in the future to test the model at the hillslope scale using the data gathered in the artificial sprinkling experiments. Our results are applicable to other study sites, and would be an interesting asset to be tested against high-frequency transport and solute data.

This work suggests that the subsurface structures can control rainfall-runoff response. A logical follow-up to this could include a subsurface map obtained from multiple ERT surveys at the experiment site, as well as more groundwater wells to provide spatially-distributed information on subsurface saturation, and to explore whether surface or bedrock topography are responsible for the subsurface flow contribution to discharge. Such information could be used to test the suggested structure hereby proposed, where the response might be related to a distinctive subsurface flow system, with a prevalent flow direction in the soil layer (vertical) and
bedrock (laterally oriented fractures, due to cleavage), with the deeper groundwater body, within the bedrock.

The framework applied here showed a lack of strong relationships between celerity and antecedent wetness conditions (e.g. storage deficit, antecedent moisture and precipitation), and could be related to the distance metrics chosen to define celerity. These results might be explored in the context of fill and spill, in that even if celerities do not seem strongly related to wetness, there might be some threshold of connectivity/runoff coefficient to be explored. This would then mean that effective upslope distance is less under dry conditions than under wet, and celerity would appear larger than it really is using the fixed distance definition.

Within the process of evaluating velocity and celerity responses we should also include a more detailed analysis of the double peaks, which are difficult to identify but which suggest that, on occasions hillslope contributions to the hydrograph may be more significant. Resolution of the celerity/velocity relationship remains an open question and one that may be approached using multiple catchment investigations, improved velocity estimates (from high-frequency tracer sampling and or injection), as well as exploring these and other distance metrics.
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It is then, and only then, that you will find the wonderland”

L. Carrol

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