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Key Points:
- Differences in soil water and drainage samples are caused by preferential pathways
- Differences in chemical versus isotopic tracers highlight the effect of plant uptake
- Need for additional tracer experiments where the tracers are sampled from within the plant

Supporting Information:
- Supporting Information S1
- Software S1
- Data Set S1
- Data Set S2
- Data Set S3
- Data Set S4

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Velocities, Residence Times, Tracer Breakthroughs in a Vegetated Lysimeter: A Multitracer Experiment

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Abstract Flow velocities, residence times, and tracer breakthroughs at the lysimeter scale are affected by matrix properties and preferential flow. Despite their relevance to transport processes, however, the relative timing of preferential flow, and its link to transit times through the soil block, is still poorly described. Here we present and analyze tracer data from a 2.5 m^3 vegetated lysimeter experiment where 18 mm of isotopically labeled water was added as a pulse and then followed with a series of tracer-free controlled rainfall events for 5 months. A solution of two fluorobenzoid acid tracers was also injected and tracked. Time series of soil water samples at three different depths and bottom drainage samples were collected and analyzed. Unlike past lysimeter experiments, a willow tree grown within the lysimeter exerted strong evapotranspiration fluxes. By comparative analysis of soil water and bottom drainage samples, we show the presence of both translatory and preferential flow features reflecting the interplay of slow vertical percolation and fast recharge through macropores. We found that water ponding and evaporating from the top of the lysimeter after irrigation prompted samples to be highly and irregularly fractionated. Comparative analyses of multitracer breakthroughs (adjusted by removing fractionation effects) showed that fluorobenzoid acid tracers reached the bottom of the lysimeter earlier than the isotopes, likely due to the effect of plant uptake. Our results underscore the essential role of models to interpret tracer behavior and, critically, the importance of future experiments aimed at measuring the ages of the water abstracted by vegetation.

1. Introduction

Despite many decades of study of the velocities, residence times, and tracer breakthroughs, major gaps in our ability to measure, understand, and model such processes exist. Early 1-D tracer soil experiments at the core and plot scale with tritium by Zimmermann, Ehhalt, et al. 1967, Zimmermann, Münnich, et al. 1967, and Horton and Hawkins (1965) revolutionized the field of hillslope hydrology by showing the translatory, piston flow behavior as rain migrated vertically through soil cores. Such work became the foundation of the variable source area concept by Hewlett and Hibbert (1967) and influences still today how water and tracer are modeled from the soil surface to the water table. Early 1-D tracer experiments and continued use of 1-D tracer experiments with repacked soil and follow-on 2-D hillslope-scale irrigation experiments (e.g., Graham et al., 2010; Jackson et al., 2016) have shown that while displacement occurs between events, during events, preferential flow predominates with pulses of considerable transport. For example, McGuire et al. (2007) showed in a hillslope experiment at the HJ Andrews site in Oregon that tracers applied 15 m apart on a steep wet hillslope arrived together at the slope base. Similarly, modeling work by Weiler and McDonnell (2007) at the Maimai watershed in New Zealand showed episodic breakthrough pulses during events and translatory flow of water and tracer between events. Such examples are now the rule, rather than the exception in field-based tracer tests.

But while tracer tests expand to new locations and models go from conceptual- to physics-based (Laine-Kaulio et al., 2014; Sprenger et al., 2018), these separate and combined matrix and preferential flow behaviors and their control on the resulting velocities, residence times, and tracer breakthroughs have been exceedingly difficult to distinguish and isolate until now (Guo & Lin, 2018), and have frustrated model attempts and quantitative descriptions in cores and hillslopes where boundary conditions have not been able to be controlled (Rodhe et al., 1996; Sprenger et al., 2016) at the scale of interest.

This is important because of the links between water age and hydrochemistry (Benettin et al., 2017; Kirchner, 2003; McGuire & McDonnell, 2006; Rinaldo et al., 2015; Soulsby et al., 2009; Tetzlaff et al., 2015; Weiler et al., 2003). We know at the catchment scale that much of the storm runoff seen in the stream is released "stored water" that existed in the catchment for days to years before the event (Kirchner et al., 2003; McDonnell et al., 2007; McDonnell & Beven, 2014; Stewart & McDonnell, 1991). We still lack the full hydrological theory to unpack all this and to reconcile empirical evidence with the dynamic character of hydrologic flows.

How long water and solutes are stored and mixed—chiefly in the subsurface storage (Botter et al., 2010; Benettin et al., 2015; Harman, 2015; van der Velde et al., 2012)—is a major research question. While there have been recent calls to come to grips with these issues (McDonnell & Beven, 2014) and recent theoretical work on the different ages of groundwater, plant water uptake, and streamflow (Botter et al., 2011; Berghuijs & Kirchner, 2017), little progress has been made experimentally due to the extreme measurement difficulty. So how can we make progress in understanding the processes first explored with tracer tests in the mid-1960s in light of new understanding of the velocities, residence times, and tracer breakthroughs? Here we present new flow and transport data from a large vegetated lysimeter. Large weighing lysimeters (e.g., Pütz et al., 2016; Young et al., 1996) are one method to investigate transport in soils (e.g., Gebler et al., 2015; Groh et al., 2018; Kim et al., 2016; Stumpp, Maloszewski, et al., 2009; Stumpp et al., 2012) because they facilitate instrument installation and allow precise estimates of storage and fluxes in/out of the soil core. Indeed, such experiments now dominate many national measurement programs like TERENO (http://teodoor.icg.kfa-juelich.de), where more than 120 such weighing lysimeters are now in operation. Manipulation experiments often require stressing some of the environmental conditions (e.g., the use of abundant irrigation to increase solute recovery or the confinement of tree roots in a potentially small soil volume), but the flexible experimental design and the possibility to use multiple tracers and several observation points allows targeting a broad range of hydrologic problems.

Future lysimeter studies should build more realism into the experimental setup via tree growth, tree-induced soil structural development, and root distribution to allow preferential flow networks to evolve naturally within the lysimeters over many years and many natural rainfall cycles. We present new experiments from such a forested 2.5 m^3 vegetated lysimeter at the École Polytechinque Fédérale de Lausanne (EPFL) lysimeter site in Switzerland. We build on Queloz, Bertuzzo, et al. (2015) who performed a series of lysimeter experiments to investigate the effect of precipitation variability on tracer transport. We show new results using multiple tracers that help quantify the impact of preferential flow on tracer transport. Unlike past work, we focus on tracking the tracer simultaneously in the soil and at the bottom outlet of the lysimeter, to highlight the structural differences between the two. We achieve this using chemical and stable isotope tracing of the water input that shows, additionally, the possible effect of plant uptake on tracer transport. We test the null hypothesis that all flow into and through the lysimeter is simple displacement. We quickly reject this hypothesis and explore the following key questions:

1. Can we detect isotope fractionation of the added tracer in the soil water and if so, how does it affect our understanding of mixing processes?
2. Do different tracers show different breakthrough curves? And if so, how, where, and why?
3. What are the relative transport velocities revealed by soil water samples internal to the lysimeter and drainage samples that seep out the bottom of the lysimeter?

The paper is organized as follows. Section 2 describes the experimental setup, including its specific design and operational differences with earlier tests by Queloz, Bertuzzo, et al. (2015) and the data analysis pursued. Section 3 presents the main Results. Section 4 provides a discussion that starts with the early statistical rejection of the simple displacement assumption and then focuses on the fractionation of the isotopic tracers and the implications of the differences observed in the tracer breakthrough curves. Particular emphasis is placed

on the characterization of transport throughout the manuscript. Finally, section 5 presents the Conclusions and perspectives of critical future needs of the experimental and theoretical research needs.

2. Methods

2.1. Experimental Setup

Queloz, Bertuzzo, et al. (2015) initiated a set of lysimeter experiments within the EPFL campus in Lausanne (CH), between May 2013 and July 2014. We build upon that work and focus here on a 5-month period between February and July 2014. The period was characterized by the one-time application of chemical and isotopic tracers and their breakthrough within and out of the soil column base.

The lysimeter has a surface area of 1.12 m^2 and a depth of 2.5 m, all supported by three load cells. The lysimeter is filled with sandy soil (roughly 50% loamy sand and 50% lacustrine sand) and was planted in 2012 with two small willow trees (*Salix viminalis*). The trees had a height of approximately 2 m at the time of the experiment and although their root distribution was not characterized, significant amounts of roots of different sizes were found at any depth. A translucent gable roof placed under the tree canopy was used to prevent natural rainfall from entering the soil, but allowed the plants to be exposed to natural ambient conditions. At the bottom of the lysimeter, a water table was maintained in a 50-cm deep gravel filter to mimic the presence of an underlying aquifer. The water table was maintained through a syphon in the drainage pipe that prevented percolation when the water table was equal to or lower than 200-cm deep. No water was added to keep the water table at a fixed depth. The lysimeter was manually irrigated with tap water through the experiment. The irrigation regime followed a predefined routine aimed at reproducing natural precipitation, with designed sequences of dry and wet spells. Irrigation water would sometimes pond at the surface for up to 30 min. Water was likely exposed to evaporation in case the irrigation routine required application of water during dry sunny days.

The tracer application was characterized by a single labeled irrigation of about 18 mm with an isotopic composition ($\delta^{18}O = 0.97‰$, $\delta^{2}H = 6.3‰$) that was markedly different from the water used for regular irrigation (approximately $\delta^{18}O = -12.3‰$, $\delta^{2}H = -90‰$). The labeled irrigation consisted of distilled sea water, collected from the "Acqua Alta" offshore platform (courtesy of Roberto Zonta, National Research Council, Italy) in the Gulf of Venice. Additionally, the isotopically labeled water pulse was also marked with two difluorobenzoic acids (2,5-DFBA and 2,6-DFBA, here termed TR1 and TR4) at a concentration of 100 mg/L. The labeled water pulse was applied 2 days after previous nonlabeled irrigation.

The labeled irrigation was tracked by taking soil water samples and bottom drainage samples for 140 days after the tracer application. During a sampling day, soil water samples were collected through suction cups, at a pressure of −0.6 bar that was maintained for 4–6 hr via an automated pump. Initially, three suction cups (A, B, and C) were installed at each of three different depths (50, 100, 150 cm). But in the end only a total of six cups fully performed throughout the experiment (cups 50B and 100B did not work and cup 150B only allowed collection of very small water volumes). On average, a soil water sample was collected every 5 days from each depth, making a time series of 27 samples per depth. Drainage from the lysimeter base was collected via an automatic sampler in a flow-proportional mode. An acquisition failure caused the loss of 2 weeks of data between May and June. On average, two samples were collected each day making a total of 241 samples. After collection, samples were filtered by 0.45 μm hydrophobic syringe filters, placed in 3 ml glass vials with septum screw caps and then stored at 4 °C until analysis. Measurements of $\delta^{2}H$ and $\delta^{18}O$ were made using a Cavity Ring Down Spectrometer L2130-*i* (Picarro, United States) at the CEL laboratory at EPFL.

All hydrologic and fluorobenzoid acid (FBA) data can be found in Queloz, Bertuzzo, et al. (2015). Isotope data are unpublished and they are provided here as supporting information material.

2.2. Data Analysis

For both the isotopes and the FBA tracers, we computed a mean solute/isotopic concentration for each soil depth by averaging measurements at the same depth from different suction cups (arithmetic average). One suction cup (150 cm depth, sector B) was excluded from the computation because the extracted volume was much lower than the others. Individual measurements compared to the depth-mean (reported in Figures S2 and S3) show that, while measurements display some differences in variability and timing (as expected in a heterogeneous environment), the breakthrough curves are consistent at each depth and significantly different from the curves at different depths. Hence, the resulting average curves are considered as indicative of the behavior at each depth for all the following analyses.

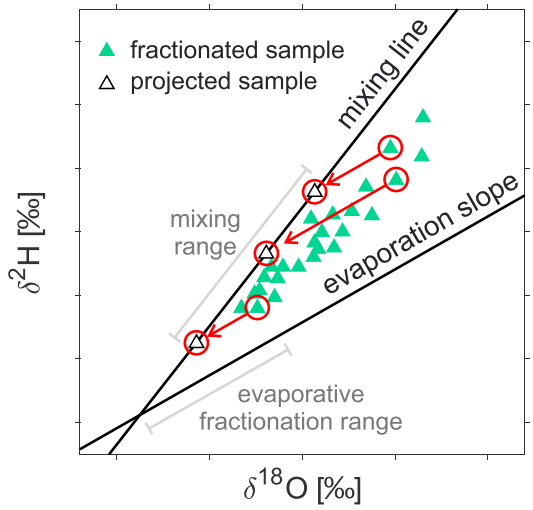

Figure 1. Conceptual plot showing how to separate the effect of source mixing and evaporative fractionation for a water sample. In dual-isotope space, the samples can be projected onto the mixing line by following a trajectory parallel to the evaporation slope. This identifies the mean source for that sample. In the lysimeter experiment, this mean source represents the degree of mixing between the two sources (labeled irrigation pulse and regular tap water). The same procedure can be used to project samples on an evaporation slope and estimate the range of evaporative fractionation.

We computed normalized concentration breakthrough curves (NBTC) in the bottom drainage as

$$\mathrm{NBTC}\,(t) = \frac{C_Q(t) - C_0}{(C_I(t_0) - C_0)\,I(t_0)}, \tag{1}$$

where I represents the volume (mm) of injected water, C_Q is the measured solute/isotopic concentration in the bottom drainage, C_0 is the initial concentration already present (if any) in the lysimeter, and C_I is the concentration of the labeled irrigation. The term C_0 is necessary whenever some background tracer concentration is already present in the system. For the FBA tracers, $C_0 = 0$. For the isotopes, C_0 was measured from soil water samples taken at the very beginning of the experiment. Equation (1) equally applies to mass concentrations (e.g., expressed in mg/L) and isotope delta notation (expressed in ‰) and results in curves with units of mm^{-1}. The advantage of using these normalized curves is that they allow comparisons among different solutes/tracers injected in different amounts. Note that the NBTC may look like a transit time distribution, but, if flow is nonstationary, then transit time computations (as well as mass recovery) must be done on the mass breakthrough curve and not on the concentration breakthrough curves. Hence, they must be multiplied by flow.

Both mixing and fractionation can influence the isotopic composition of a water sample, and isolating these effects can be useful to identify the hydrologic and physical processes that influence the sample composition. When both water stable isotopes are available, this separation can be achieved, in the first place, through a simple geometric approach, as illustrated in Figure 1. In dual-isotope space, the isotopic composition of a water sample identifies a point (green triangles in Figure 1). Additionally, one can draw a "Local Meteoric Water Line" (LMWL), representing the possible compositions of meteoric waters (in this case, irrigation waters). As any mixture of precipitation sources lays on the LMWL, this can be interpreted as a "mixing line." Similarly, one can determine the slope of the evaporation line for the particular location and atmospheric conditions (e.g., following the approach by Gat & Gonfiantini, 1981). Then, using elementary algebra, one can project each samples' composition onto the mixing line following a trajectory parallel to the evaporation line (red arrows). The resulting projected sample (black empty triangle in Figure 1) indicates the composition of the nonfractionated water mixture that is the mean source of the measured sample. For our pulse tracer experiment, the mean composition represents the degree of mixing between the tap water and the labeled irrigation, regardless of how much the different samples have been fractionated. By analogy, one could also project the original sample onto the evaporation line and determine the degree of fractionation (and hence the amount of evaporation) experienced by each sample, regardless of how much it has been mixed.

The LMWL in this experiment coincides with the mixing line that connect the two input sources to the lysimeter (the almost constant tap water composition and the labeled irrigation water). The evaporation line slope,

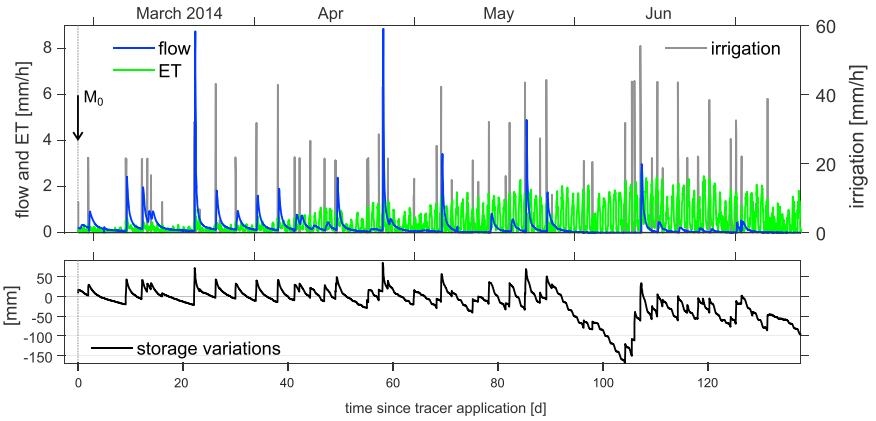

Figure 2. Measured hydrologic fluxes and storage variations in the lysimeter during the experiment. The experiment was run under rather wet conditions, although transpiration after April rapidly abstracted large amounts of water and resulted in quick water storage depletion (see, e.g., late May).

needed to apply the projection method, was obtained following the approach and numerical code of Benettin et al. (2018). Under the assumption that the vapor composition under the plastic roof was in equilibrium with the regular irrigation water, and using the mean temperature (8°) and relative humidity (0.7) recorded at a nearby weather station, the resulting mean evaporation slope is roughly 3.2. This is consistent with the isotopic composition of unmixed samples taken from the soil and lysimeter drainage water at the beginning of the experiment. The inferred evaporation slope can change slightly if different parameters and assumptions are used in the computations. However, we found that small variations had negligible effect on the results.

The MATLAB code used for all the data analysis and figures is provided as supporting information material.

3. Results

The hydrologic fluxes and the water storage variations in the lysimeters during the 5 months after the labeled irrigation are illustrated in Figure 2. During this period, the lysimeter received a total of 2,200 mm of (nonlabeled) irrigation water and "lost" 812 mm through the base drainage and 1,500 mm to evapotranspiration. These relatively high fluxes are a consequence of the particular design of the experiment, which aimed to investigate the transport of different tracers subject to the same hydrologic conditions and to increase the

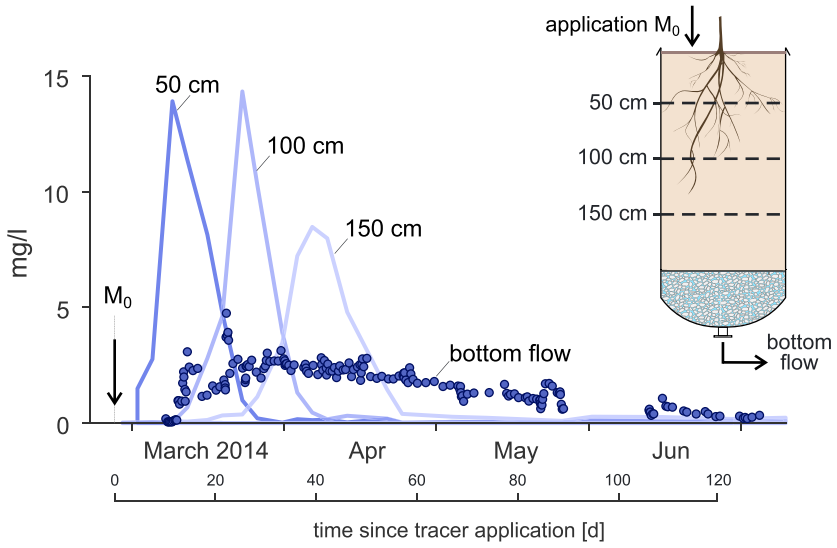

Figure 3. Concentration breakthrough curves for Tracer 4 (2,6-DBFA) obtained for the lysimeter base drainage and for soil water samples extracted at 50, 100, and 150 cm depths. The inset cartoon illustrates the general experimental setting (but not the actual rooting system of the willow tree).

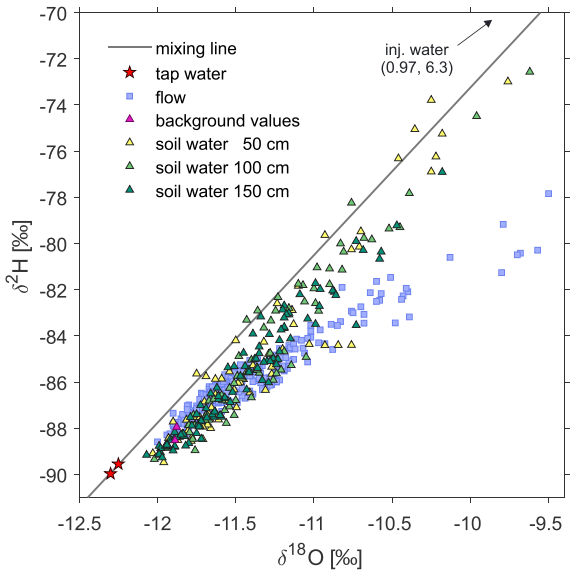

Figure 4. Dual-isotope plot showing all flow and soil water samples. The "mixing line" connecting the irrigation tap water and the labeled water pulse ($\delta^{18}O = 0.97‰$, $\delta^{2}H = 6.3‰$) has a slope of 7.3.

recovered tracer mass. While the hydrologic conditions during the experiment were rather wet, willow transpiration after April resulted in a rapid dry-down within the lysimeter. Figure 2 shows that the total water storage and the bottom drainage are characterized by large event-based fluctuations induced by the nonstationary irrigation regime.

FBA Tracers 1 and 4 showed similar breakthrough behavior but different total recoveries at the lower outlet (45% for TR1 and 69% for TR4). Figure 3 shows the concentration of Tracer 4 in soil water (at the three different depths) and in the lysimeter drainage. Tracer 1 is not shown in Figure 3 because it had essentially the same behavior, with slightly lower concentrations. All soil water samples followed an advection-dispersion type of transport, with the breakthrough curves damped with depth. Although irrigation inputs were irregular, the FBA tracers consistently took about 15 days to move an average distance of 50 cm. Despite this and despite the damping effect of the saturated water volume at the bottom of the lysimeter, some of the tracer arrived quickly at the lysimeter base. The first detection of Tracer 4 in the bottom drainage (at 250 cm depth) coincided with the first detection in the 100 cm soil suction cups and well before the tracer was found at the deepest suction cups at 150 cm. This first result suggests that the suction cups do not intercept preferential pathways. Nevertheless, these preferential flow pathways represent an important component of the drainage flow from the lysimeter base.

The isotopic composition of all water samples is shown in dual-isotope space in Figure 4 (and as time series in Figure S1). In the dual-isotope plot, the mixing line connecting the tap water and the labeled irrigation has a slope of 7.3. Almost all the samples plot below such mixing line, indicating that they have undergone significant evaporative fractionation. Note that early "background" samples (purple triangles in Figure 4), taken at the beginning of the experiment, are unaffected by mixing with the spiked irrigation. They plot away from their source tap water (red stars). All other samples are influenced by both fractionation, which causes samples to be heavier and to plot below the mixing line, and by mixing with the heavy labeled irrigation, which causes samples to move along the mixing line. However, there are marked differences between sample types: in the case of soil water samples, the degree of fractionation (represented by the vertical distance to the mixing line) is rather constant and without noticeable differences among the different depths; in the case of flow

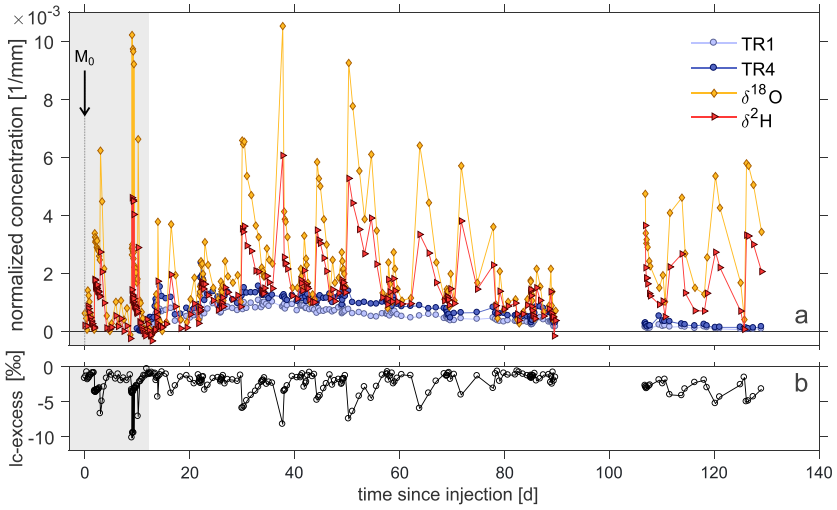

Figure 5. (a) Normalized concentration breakthrough curves in the bottom drainage for all isotopic and fluorobenzoid acid tracers; (b) lc-excess time series (lowest lc-excess values indicate the times when the samples were most fractionated). The gray area in the background indicates the period before the first detection of the fluorobenzoid acid tracers and suggests that drainage water had been exposed to evaporative fractionation before the labeled irrigation was applied.

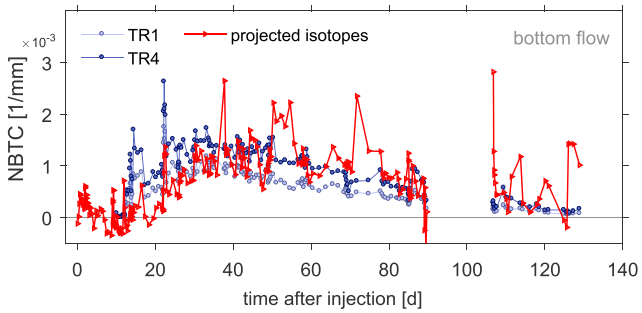

Figure 6. Normalized concentration breakthrough curves in the bottom drainage for all the tracers. The red curve indicates the single isotope NBTC obtained after removing the effect of evaporative fractionation. Although some noise in the isotope values remains, the NBTC of the different tracers are now comparable. NBTC = normalized concentration breakthrough curves.

samples, instead, heavier samples are also more fractionated. This behavior is not attributed to measurement errors, as results are consistent across duplicate samples and lab analyses were run on batches that included both soil water and drainage water samples. The observed fractionation patterns can be explained considering that fractionation likely occurred whenever heavy irrigation took place during a dry sunny day. In such a case, ponded water on top of the lysimeter would fractionate and then it would propagate vertically toward the bottom outlet of the lysimeter through preferential flow, ultimately influencing bottom drainage samples more than soil water samples.

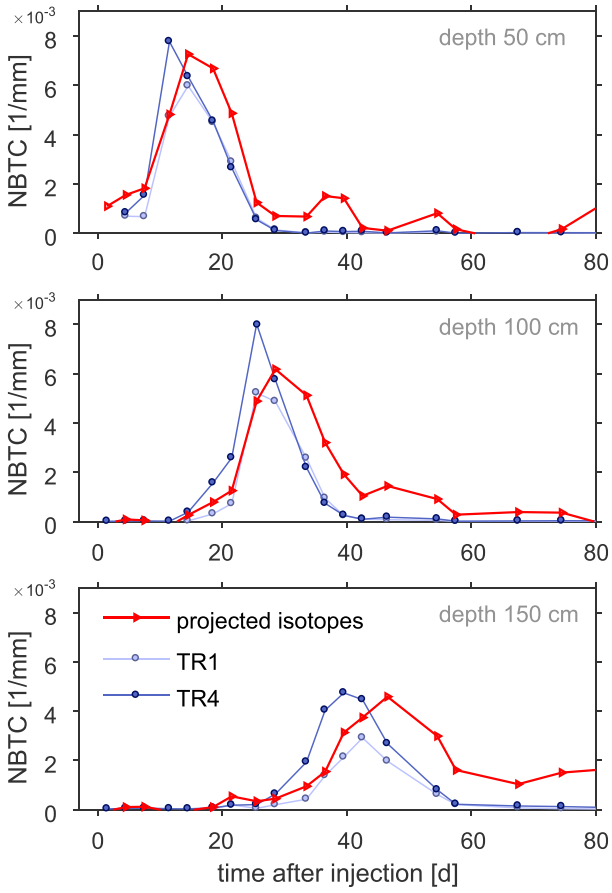

Figure 7. NBTC in the soil water for all the tracers. The red curve indicates the single isotope NBTC obtained after removing the effect of evaporative fractionation. NBTC = normalized concentration breakthrough curves.

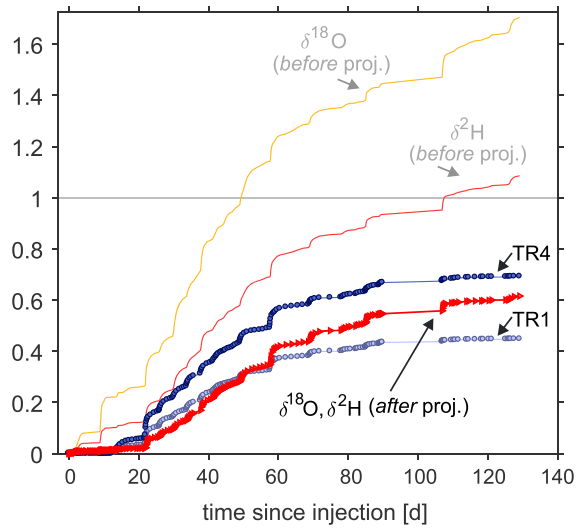

Figure 8. Normalized tracer mass recovery in the bottom drainage. Due to fractionation of irrigation water, the labeled pulses of ^{18}O and ^{2}H have an apparent recovery greater than 100%. When the effect of fractionation is removed using a geometrical projection (section 2.2), the isotope recovery is reduced to 62% is consistent with possible partitioning between leakage and evapotranspiration. The temporal dynamics of TR1 are very similar to those of TR4, but the recovery is lower (45% and 69%, respectively).

All breakthrough curves in the drainage from the lysimeter base are compared in Figure 5. The upper plot shows the NBTCs while the lower plot reports the time series of an isotope fractionation indicator (the "lc-excess," proposed by Landwehr and Coplen (2006), where negative values indicate the occurrence of kinetic fractionation).

The NBTCs of the isotopes are dominated by large and intermittent spikes, but the bottom envelope of the curves is very similar to the breakthrough of the FBA tracers. This suggests that the envelope represents the actual transport of the labeled irrigation to the lysimeter base (and it quantifies mixing of the labeled irrigation with ordinary irrigation), while the spikes indicate the effect of the occasional strong fractionation on the breakthrough curve. The NBTC of $\delta^{18}O$ is generally higher than that of $\delta^{2}H$ and isotope samples that depart most significantly from the FBA curves are also the most fractionated ones. This is shown by the lc-excess time series that mirrors the large spikes of the isotopes NBTC. The spiky behavior indicates that fractionation occurred irregularly in time and magnitude. Further comparisons between the isotopes and the FBA curves show that fractionation occurred also before the arrival of the labeled irrigation to the bottom of the lysimeter (period marked by a gray rectangle in Figure 5), suggesting that fractionation occurred in the "regular" irrigation water throughout the experiment, including the period preceding the application of the tracers.

When fractionation is filtered-out using the projection approach described in section 2.2, the NBTCs of $\delta^{18}O$ and $\delta^{2}H$ collapse into a single curve. Such a curve is similar to those of the FBA tracers for both the bottom drainage (Figure 6) and soil water (Figure 7). Indeed, the majority of the spikes that characterized the isotopic signal of the lysimeter drainage became much lower or were even completely removed. Although important differences with the FBA curves remain (see section 4.2), all NBTCs are now comparable.

Tracer recovery at the lysimeter drainage, obtained by multiplying the NBTCs by the drainage flow, is shown in Figure 8. The two FBA tracers had similar dynamics but different total recoveries (45% for TR1 and 69% for TR4). The original isotope curves are heavily affected by fractionation causing their apparent recovery to be higher than 100%. This is obviously unrealistic and it is due to mixing with heavily fractionated irrigation waters throughout the experiment. After the effect of fractionation is removed (red curve in Figure 8), isotope recovery is reduced to 62%, in keeping with the FBA measured recoveries. We note that the actual isotope recovery may be higher still as the isotope breakthrough had not leveled off fully by the end of the experiment.

4. Discussion

Water flow through the soil core is characterized by the interplay between slow vertical percolation and fast recharge flow through macropores. The degree of mixing between these two major mechanisms is key to

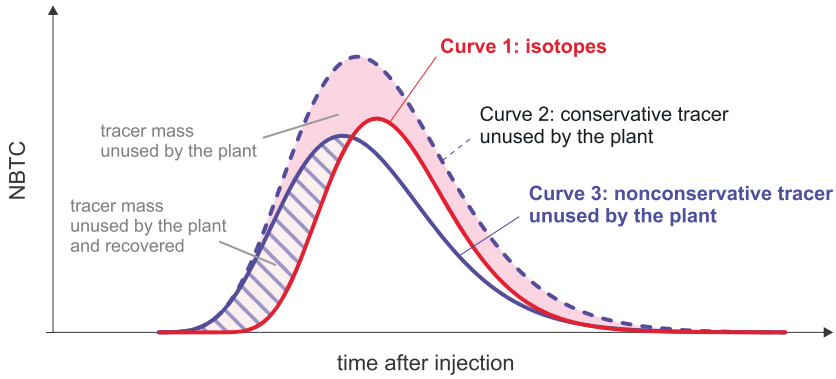

Figure 9. Conceptual illustration of the concentration breakthrough of different tracers. Isotopes (Curve 1) are passive to plant uptake, so their recovery is <100%. Conservative tracers that are not subject to uptake by vegetation (Curve 2) would have an ideal recovery of 100%. The difference between Curve 2 and Curve 1 could quantify the tracer mass unused by the plants. However, most tracers are not fully conservative (Curve 3) and not all the mass is recovered at the outlet. If plant uptake and degradation effects are not uniform over the breakthrough, Curve 1 and Curve 3 may be shifted in time.

understand the partitioning of soil water into evapotranspiration and recharge and to infer its transit times. Our multitracer experiment shows that flow and transport through our vegetated soil core cannot be solely explained by vertical displacement, since the tracer observations in the soil water samples and at the lower lysimeter outlet were often at odds with one another. Such a dual flow and transport behavior was shown in the chemical tracers (Figure 3) and in the stable isotope tracing (Figure 4).

4.1. Can We Detect Isotope Fractionation of the Added Tracer in the Soil Water and if so, How Does it Affect our Understanding of Mixing Processes?

Our lysimeter setup caused irrigation water to often pond on top of the lysimeter and be exposed to evaporation. This effect was likely enhanced for larger irrigation events, which also produced larger infiltration volumes. As a consequence, water samples (particularly bottom drainage ones) were highly and irregularly fractionated (Figure 5). The early strong fractionation of the injected waters effectively masked any further fractionation associated with soil water evaporation within the soil core. Therefore, we are only able to explain the marked differences between soil water and drainage samples in the context of how the fractionation signal was transported through the column and not to where the fractionation took place.

In this experiment, isotopes were not good tracers of mixing processes until fractionation effects were removed (Figures 6–8). Evaporative fractionation in typical lysimeters (Stumpp, Stichler, et al., 2009) and field studies (Sprenger et al., 2017) is often not as high and irregular as in our experiment. But even low amounts of fractionation generate an increase in isotope values that can corrupt the analysis of the isotopic time series. Hence, some removal of fractionation effects is needed to study mixing and transit times whenever a water sample shows evidence of fractionation. Note that in this study we did not explore the uncertainty in the isotope projection approach, as it would go beyond the purpose of the analyses. But more advanced mixing analyses could be done using the Bayesian approach proposed by Bowen et al. (2018), which takes into account the uncertainty in fractionation processes, precipitation composition, and isotopic measurements.

4.2. Do Different Tracers Show Different Breakthrough Curves? And if so, How, Where and Why?

Figures 6–8 show that, although the different tracers have a comparable behavior and recovery, important differences remain among the breakthrough curves. FBA tracers could provide a cleaner breakthrough because of their lack of any background concentration. Previous experience with these tracers (Queloz, Bertuzzo, et al., 2015) also showed that while FBAs were fully conservative under laboratory column experiments, they were partially degraded in unsaturated field conditions. Isotope values are more uncertain due to their natural abundance and variability in the soil water and irrigation water, but they are not subject to degradation/decay. Crucially, the different tracers show different behaviors with respect to vegetation uptake. While water isotopes are usually considered as passive tracers (Ehleringer & Dawson, 1992), FBAs are largely unused by plants (Bowman et al., 1997). Examination of Figures 6 and 7 shows that the chemical tracer breakthroughs (particularly TR4) were recorded earlier than the isotopes. The same pattern is consistently observed in the breakthrough at each individual suction cup (Figure S4). This behavior was unexpected as processes that

might favor it (like anion adsorption) have not been reported for FBA tracers and retardation effects are instead more common (Seaman, 1998; Serres-Piole et al., 2011). We hypothesize that such a behavior is related to the effect of plant uptake and we provide a conceptual interpretation of our NBTCs in Figure 9.

In general, tracer BTCs are affected both by the tracer velocities and by the amount of molecules that are recovered. Even when the recovered molecules travel at the same velocity as the water carrier, different recoveries may results in an apparent acceleration/retardation of the breakthrough. When the mass of a chemical is unused by the plant, it can remain in the water that percolates downward, such that an extra amount of mass compared to the isotopes can reach the lysimeter base. This results in a recovery of the chemical tracer (dashed purple line in Figure 9) theoretically higher than that of the isotopes (red line). The difference between these two curves could be used in principle to quantify the effect of plant uptake through time. However, chemical tracers are often subject to degradation, so the actual solute recovery (solid purple line) can be significantly lower. Overall, degradation and plant uptake jointly contribute to shaping each breakthrough curve. The fact that the peak in the FBA breakthrough arrived earlier than that of the isotopes let us formulate the hypothesis that plant uptake mainly affected the tracers right after they were applied (short transit times, left tail of the NBTC), while degradation mainly affected the tracer molecules that spent longer time within the core (right tail of the NBTC). Due to the effects of solute degradation and data uncertainty (especially in the projected isotope NBTC) the available measurements only allow a qualitative assessment of the possible effect of vegetation on tracer transport. Nevertheless, the curves can be used to calibrate transport models (e.g., Brinkmann et al., 2018; Mali et al., 2007; Queloz, Carraro, et al., 2015; Stumpp, Nützmann, et al., 2009; Sprenger et al., 2018) and estimate water velocities, also tackling a number of problems like the partitioning between evapotranspiration and recharge flows and the related residence times. The inability to quantify the effects of plant uptake by only looking at the residual tracer in the soil column points to the need for new experiments where plant uptake is directly monitored (Brinkmann et al., 2018), for example, through the collection of xylem water samples (see also section 4.4).

4.3. What are the Relative Transport Velocities Revealed by Soil Water Samples Internal to the Lysimeter and Drainage Samples That Seep out the Bottom of the Lysimeter?

Our multitracer irrigation with isotopically labeled water and two different FBA tracers shows that drainage water from the lysimeter base is strongly affected by the presence of preferential pathways, while soil water samples appear more representative of slower percolation through the soil matrix. After application, all the tracers took around 35–40 days to be first recorded in soil water at 150 cm depth (Figure 7), while they only needed 15–20 days to be found in the bottom drainage at 250 cm depth (Figure 6). In this sense, suction cups only traced the remainder of what had percolated through the column. Although soil water samples were collected at lower frequencies that might have inhibited the detection of preferential flow, the tracer breakthroughs occurred over periods of more than 30 days, hence it seems unlikely that sampling at higher frequency would significantly modify this pattern. Drainage samples were also more heavily fractionated than soil water samples because of the fast transport of fractionated water that had ponded on top of the lysimeter. Isotope recovery suggests that roughly 30–40% of the labeled irrigation returned to the atmosphere through the willow tree transpiration and soil evaporation, while the remaining 60–70% took about 5 months to be fully flushed out of the soil column. Given the high temporal variability of transport processes, we expect very different recoveries for water pulses applied in different times of the year or under different hydrologic conditions.

The main implication of these results is that tracer velocities may appear very different if assessed from soil suction cups or from bottom drainage only. The observed divergence in flow velocities was likely enhanced by the lysimeter setting, where the very wet conditions and the possible disturbances of the lysimeter walls may have increased the impact of preferential pathways. Nevertheless, the experiment highlights the difficulty in intercepting macropores using suction cups. This is particularly relevant for field studies (see Penna et al., 2018), where macropores are difficult to intercept and recharge fluxes cannot be collected. In such circumstances, the estimate of water velocity in soils based on low-frequency measurements from suction cups is likely to miss the fast flow components and therefore underestimate the actual transit times.

4.4. Next Steps

Beyond the preferential flow from the base of the lysimeter, many have noted (Rinaldo et al., 2015; Soulsby et al., 2016) that the process of evapotranspiration directly impacts the chemical and isotopic composition of soil water storage, with direct consequences for stream water quality. Experimental evidence (e.g., Brooks

et al., 2010) has revealed significant differences between the isotopic composition of stream water and xylem water, leading to the "two water worlds" concept (Evaristo & McDonnell, 2017; McDonnell, 2014), but conclusive experimental evidence is missing on vegetation affinity for uptake of waters of different ages. Our work suggests new experiments that are needed to measure directly within the tree, the tracer uptake, and the time varying age of xylem water. For this lysimeter and other experimental locations where one is able to go after such fundamental questions, the next step is to quantify the exit age distribution of these dual preferred flows and their relation to the slower flow in the soil matrix.

5. Conclusions

Results from our multitracer experiment conducted in a large vegetated lysimeter lead to the following conclusions:

- Tracer transport through the soil column cannot be solely explained by simple displacement flow. Hence, transport dynamics are incomplete when assessed through soil water samples or drainage samples only.
- Bottom drainage samples were strongly influenced by preferential pathways. The labeled irrigation was recorded in the drainage flow at 250 cm depth well before it was observed in the soil water at 150 cm depth. The isotopic signal of the bottom drainage also had a rather different isotopic composition than soil water samples.
- Due to the particular experiment design, isotope fractionation likely occurred right after heavy irrigation, when ponding water remained exposed to evaporation. In such cases, waters with highly fractionated isotopic composition propagated quickly toward the lysimeter bottom, influencing the drainage isotopic composition more than the soil water composition.
- Both isotope mixing and fractionation cause the isotopic composition of a sample to increase, but the two effects can be separated using a simple projection methodology explained in section 2 and further illustrated in the attached numerical code.
- After the effect of fractionation is removed, the different tracers have comparable behaviors. Still, the residual differences in the tracer breakthrough curves (especially in the left tail) suggest that selective plant uptake may cause an apparent acceleration/retardation of the tracer recovery.
- Isotope recovery indicates that approximately 30–40% of the labeled irrigation returned to the atmosphere via evapotranspiration. The remaining 60–70% was released through the bottom outlet over roughly 5 months.

Overall, our results call for new controlled experiments where the tracer composition in the plant uptake is specifically targeted.

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References

Benettin, P., Bailey, S. W., Rinaldo, A., Likens, G. E., McGuire, K. J., & Botter, G. (2017). Young runoff fractions control streamwater age and solute concentration dynamics. *Hydrological Processes*, *31*(16), 2982–2986. https://doi.org/10.1002/hyp.11243

Benettin, P., Rinaldo, A., & Botter, G. (2015). Tracking residence times in hydrological systems: Forward and backward formulations. *Hydrological Processes*, *29*, 5203–5213.

Benettin, P., Volkmann, T. H. M., von Freyberg, J., Frentress, J., Penna, D., Dawson, T. E., & Kirchner, J. W. (2018). Effects of climatic seasonality on the isotopic composition of evaporating soil waters. *Hydrology and Earth System Sciences Discussions*, *2018*, 1–16.

Berghuijs, W. R., & Kirchner, J. W. (2017). The relationship between contrasting ages of groundwater and streamflow. *Geophysical Research Letters*, *44*, 8925–8935. https://doi.org/10.1002/2017GL074962

Botter, G., Bertuzzo, E., & Rinaldo, A. (2010). Transport in the hydrologic response: Travel time distributions, soil moisture dynamics, and the old water paradox. *Water Resources Research*, *46*, W03514. https://doi.org/10.1029/2009WR008371

Botter, G., Bertuzzo, E., & Rinaldo, A. (2011). Catchment residence and travel time distributions: The master equation. *Geophysical Research Letters*, *38*, L11403. https://doi.org/10.1029/2011GL047666

Bowen, G. J., Putman, A., Brooks, J. R., Bowling, D. R., Oerter, E. J., & Good, S. P. (2018). Inferring the source of evaporated waters using stable H and O isotopes. *Oecologia*, *187*(4), 1025–1039. https://doi.org/10.1007/s00442-018-4192-5

Bowman, R. S., Schroeder, J., Bulusu, R., Remmenga, M., & Heightman, R. (1997). Plant toxicity and plant uptake of fluorobenzoate and bromide water tracers. *Journal of Environmental Quality*, *26*(5), 1292–1299.

Brinkmann, N., Seeger, S., Weiler, M., Buchmann, N., Eugster, W., & Kahmen, A. (2018). Employing stable isotopes to determine the residence times of soil water and the temporal origin of water taken up by Fagus sylvatica and Picea abies in a temperate forest. *New Phytologist*, *219*, 1300–1313. https://doi.org/10.1111/nph.15255

Brooks, J. R., Barnard, H. R., Coulombe, R., & McDonnell, J. J. (2010). Ecohydrologic separation of water between trees and streams in a Mediterranean climate. *Nature Geoscience*, *3*(2), 100–104.

Ehleringer, J. R., & Dawson, T. E. (1992). Water uptake by plants: Perspectives from stable isotope composition. *Plant, Cell & Environment*, *15*(9), 1073–082.

Evaristo, J., & McDonnell, J. J. (2017). Prevalence and magnitude of groundwater use by vegetation: A global stable isotope meta-analysis. *Scientific Reports*, *7*, 44110.

Gat, J., & Gonfiantini, R. (1981). Stable isotope hydrology. Deuterium and oxygen-18 in the water cycle (*Report*): International Atomic Energy Agency (IAEA).
Gebler, S., Hendricks Franssen, H.-J., Pütz, T., Post, H., Schmidt, M., & Vereecken, H. (2015). Actual evapotranspiration and precipitation measured by lysimeters: A comparison with eddy covariance and tipping bucket. *Hydrology and Earth System Sciences*, *19*(5), 2145–2161.
Graham, C. B., Woods, R. A., & McDonnell, J. J. (2010). Hillslope threshold response to rainfall: (1) A field based forensic approach. *Journal of Hydrology*, *393*(1), 65–76. Soil Architecture and Preferential Flow across Scales.
Groh, J., Stumpp, C., Lücke, T. A. P., Vanderborght, J., & Vereecken, H. (2018). Inverse estimation of soil hydraulic and transport parameters of layered soils from water stable isotope and lysimeter data. *Vadose Zone Journal*, *17*(1).
Guo, L, & Lin, H. (2018). Chapter two — Addressing two bottlenecks to advance the understanding of preferential flow in soils. In D. L. Sparks (Ed.), *Advances in agronomy* (Vol. 147, pp. 61–117). Cambridge, MA: Academic Press.
Harman, C. J. (2015). Time-variable transit time distributions and transport: Theory and application to storage-dependent transport of chloride in a watershed. *Water Resources Research*, *51*, 1–30. https://doi.org/10.1002/2014WR015707
Hewlett, J. D., & Hibbert, A. R. (1967). Factors affecting the response of small watersheds to precipitation in humid areas. In W. E. Sopper & H. W. Lull (Eds.), *Proceedings of the international symposium on forest hydrology* (pp. 275–290). Oxford: Pergamon Press.
Horton, J. H., & Hawkins, R. H. (1965). Flow path of rain from the soil surface to the water table. *Soil Science*, *100*(6), 377–383.
Jackson, C. R., Du, E., Klaus, J., Griffiths, N. A., Bitew, M., & McDonnell, J. J. (2016). Interactions among hydraulic conductivity distributions, subsurface topography, and transport thresholds revealed by a multitracer hillslope irrigation experiment. *Water Resources Research*, *52*, 6186–6206. https://doi.org/10.1002/2015WR018364
Kim, M., Pangle, L. A., Cardoso, C., Lora, M., Volkmann, T. H. M., Wang, Y., et al. (2016). Transit time distributions and StorAge Selection functions in a sloping soil lysimeter with time-varying flow paths: Direct observation of internal and external transport variability. *Water Resources Research*, *52*, 7105–7129. https://doi.org/10.1002/2016WR018620
Kirchner, J. W. (2003). A double paradox in catchment hydrology and geochemistry. *Hydrological Processes*, *17*(4), 871–874. https://doi.org/10.1002/hyp.5108
Kirchner, J. W., Feng, X. H., & Neal, C. (2003). Fractal stream chemistry and its implications for contaminant transport in catchments. *Nature*, *403*(6769), 524–527.
Laine-Kaulio, H., Backnäs, S., Karvonen, T., Koivusalo, H., & McDonnell, J. J. (2014). Lateral subsurface stormflow and solute transport in a forested hillslope: A combined measurement and modeling approach. *Water Resources Research*, *50*, 8159–8178. https://doi.org/10.1002/2014WR015381
Landwehr, J., & Coplen, T. B. (2006). Line-conditioned excess: A new method for characterizing stable hydrogen and oxygen isotope ratios in hydrologic systems. Isotopes in environmental studies 1, IAEA 132–135 pp.
Mali, N., Urbanc, J., & Leis, A. (2007). Tracing of water movement through the unsaturated zone of a coarse gravel aquifer by means of dye and deuterated water. *Environmental Geology*, *51*(8), 1401–1412. https://doi.org/10.1007/s00254-006-0437-4
McDonnell, J. J. (2014). The two water worlds hypothesis: Ecohydrological separation of water between streams and trees? *Wiley Interdisciplinary Reviews: Water*, *1*(4), 323–29. https://doi.org/10.1002/wat2.1027
McDonnell, J. J., & Beven, K. J. (2014). Debates on water resources: The future of hydrological sciences: A (common) path forward? A call to action aimed at understanding velocities, celerities and residence time distributions of the headwater hydrograph. *Water Resources Research*, *50*, 5342–5350. https://doi.org/10.1002/2013WR015141
McDonnell, J. J., Sivapalan, M., Vache, K., Dunn, S., Grant, G., Haggerty, R., et al. (2007). Moving beyond heterogeneity and process complexity: A new vision for watershed hydrology. *Water Resources Research*, *43*, W07301. https://doi.org/10.1029/2006WR005467
McGuire, K. J., & McDonnell, J. J. (2006). A review and evaluation of catchment transit time modeling. *Journal of Hydrology*, *330*(3-4), 543–563.
McGuire, K. J., Weiler, M., & McDonnell, J. J. (2007). Integrating tracer experiments with modeling to assess runoff processes and water transit times. *Advances in Water Resources*, *30*(4), 824–837.
Penna, D., Hopp, L., Scandellari, F., Allen, S. T., Benettin, P., Beyer, M., et al. (2018). Ideas and perspectives: Tracing terrestrial ecosystem water fluxes using hydrogen and oxygen stable isotopes – challenges and opportunities from an interdisciplinary perspective. *Biogeosciences*, *15*(21), 6399–6415.
Pütz, T., Kiese, R., Wollschläger, U., Groh, J., Rupp, H., Zacharias, S., et al. (2016). Tereno-soilcan: A lysimeter-network in germany observing soil processes and plant diversity influenced by climate change. *Environmental Earth Sciences*, *75*(18), 1242. https://doi.org/10.1007/s12665-016-6031-5
Queloz, P., Bertuzzo, E., Carraro, L., Botter, G., Miglietta, F., Rao, P. S. C., & Rinaldo, A. (2015). Transport of fluorobenzoate tracers in a vegetated hydrologic control volume: 1. Experimental results. *Water Resources Research*, *51*, 2773–2792. https://doi.org/10.1002/2014WR016433
Queloz, P., Carraro, L., Benettin, P., Botter, G., Rinaldo, A., & Bertuzzo, E. (2015). Transport of fluorobenzoate tracers in a vegetated hydrologic control volume: 2. Theoretical inferences and modeling. *Water Resources Research*, *51*, 2793–2806. https://doi.org/10.1002/2014WR016508
Rinaldo, A, Benettin, P., Harman, C. J., Hrachowitz, M., McGuire, K. J., van der Velde, Y., et al. (2015). Storage selection functions: A coherent framework for quantifying how catchments store and release water and solutes. *Water Resources Research*, *51*, 4840–4847. https://doi.org/10.1002/2015WR017273
Rodhe, A., Nyberg, L., & Bishop, K. (1996). Transit times for water in a small till catchment from a step shift in the oxygen 18 content of the water input. *Water Resources Research*, *32*(12), 3497–511.
Seaman, J. C. (1998). Retardation of fluorobenzoate tracers in highly weathered soil and groundwater systems. *Soil Science Society of America Journal*, *62*(2), 354.
Serres-Piole, C., Commarieu, A., Garraud, H., Lobinski, R., & Preud'homme, H. (2011). New passive water tracers for oil field applications. *Energy & Fuels*, *25*(10), 4488–4496.
Soulsby, C., Birkel, C., & Tetzlaff, D. (2016). Characterizing the age distribution of catchment evaporative losses. *Hydrological Processes*, *30*(8), 1308–1312. https://doi.org/10.1002/hyp.10751
Soulsby, C., Tetzlaff, D., & Hrachowitz, M. (2009). Tracers and transit times: Windows for viewing catchment scale storage? *Hydrological Processes*, *23*(24), 3503–3507.
Sprenger, M., Seeger, S., Blume, T., & Weiler, M. (2016). Travel times in the vadose zone: Variability in space and time. *Water Resources Research*, *52*, 5727–5754. https://doi.org/10.1002/2015WR018077
Sprenger, M., Tetzlaff, D., Buttle, J. M., Laudon, H., Leistert, H., Mitchell, C. P. J., et al. (2018). Measuring and modeling stable isotopes of mobile and bulk soil water. *Vadose Zone Journal*, *17*(1).
Sprenger, M., Tetzlaff, D., & Soulsby, C. (2017). Soil water stable isotopes reveal evaporation dynamics at the soil–plant–atmosphere interface of the critical zone. *Hydrology and Earth System Sciences*, *21*(7), 3839–3858.

Stewart, M. K., & McDonnell, J. J. (1991). Modeling base flow soil water residence times from deuterium concentrations. *Water Resources Research*, *27*, 2681–2693. https://doi.org/10.1029/91WR01569

Stumpp, C., Maloszewski, P., Stichler, W., & Fank, J. (2009). Environmental isotope (δ18O) and hydrological data to assess water flow in unsaturated soils planted with different crops: Case study lysimeter station "Wagna" (Austria). *Journal of Hydrology*, *369*(1-2), 198–208. https://doi.org/10.1016/j.jhydrol.2009.02.047

Stumpp, C., Nützmann, G., Maciejewski, S., & Maloszewski, P. (2009). A comparative modeling study of a dual tracer experiment in a large lysimeter under atmospheric conditions. *Journal of Hydrology*, *375*(3-4), 566–577.

Stumpp, C., Stichler, W., Kandolf, M., & Simůnek, J. (2012). Effects of land cover and fertilization method on water flow and solute transport in five lysimeters: A long-term study using stable water isotopes. *Vadose Zone Journal*, *11*(1), vzj2011.0075.

Stumpp, C., Stichler, W., & Maloszewski, P. (2009). Application of the environmental isotope δ18O to study water flow in unsaturated soils planted with different crops: Case study of a weighable lysimeter from the research field in Neuherberg, Germany. *Journal of Hydrology*, *368*(1-4), 68–78.

Tetzlaff, D., Buttle, J., Carey, S. K., McGuire, K., Laudon, H., & Soulsby, C. (2015). Tracer-based assessment of flow paths, storage and runoff generation in northern catchments: A review. *Hydrological Processes*, *29*(16), 3475–3490. https://doi.org/10.1002/hyp.10412

van der Velde, Y., Torfs, P. J. J. F., van der Zee, S. E. A. T. M., & Uijlenhoet, R. (2012). Quantifying catchment-scale mixing and its effect on time-varying travel time distributions. *Water Resources Research*, *48*, W06536. https://doi.org/10.1029/2011WR011310

Weiler, M., & McDonnell, J. J. (2007). Conceptualizing lateral preferential flow and flow networks and simulating the effects on gauged and ungauged hillslopes. *Water Resources Research*, *43*, W03403. https://doi.org/10.1029/2006WR004867

Weiler, M., McGlynn, B. L., McGuire, K. J., & McDonnell, J. J. (2003). How does rainfall become runoff? A combined tracer and runoff transfer function approach. *Water Resources Research*, *39*(11), 1315. https://doi.org/10.1029/2003WR002331

Young, M. H., Wierenga, P. J., & Mancino, C. F. (1996). Large weighing lysimeters for water use and deep percolation studies. *Soil Science*, *161*(8), 491–501.

Zimmermann, U., Ehhalt, D., & Münnich, K. O. (1967). Soil water movement and evapotranspiration: Changes in the isotopic composition of the water. In *Proceedings of the iaea symposium on the use of isotopes in hydrology, international atomic energy agency (i.a.e.a.), vienna* (pp. 567–585).

Zimmermann, U., Münnich, K. O., & Roether, W. (1967). Downward movement of soil moisture traced by means of hydrogen isotopes. In G. E. Stout (Ed.), *Isotope techniques in the hydrologic cycle* (Vol. 11, pp. 28–36). Washington, D. C.: American Geophysical Union (AGU). https://doi.org/10.1029/GM011p0028