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Isotopic offsets in throughfall and stemflow may have small effects on estimates of winter precipitation fractions

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Abstract

Forest canopies alter the amount and isotopic composition of precipitation reaching the forest floor. Thus retention, evaporation and transport processes in forest canopies, and their effects on water isotopes, are key to understanding forest water cycling. Using a two-year isotope dataset from a mixed beech/spruce forest in Zurich, Switzerland, we assessed the isotopic offsets between precipitation, throughfall and stemflow. We also analysed how these offsets affect estimates of the fraction of soil water that is derived from winter precipitation. Throughfall was typically enriched in heavy isotopes compared to precipitation, but isotopically lighter than stemflow, with average δ^2H of −64.3 ‰, −59.9 ‰ and − 56.3 ‰ in precipitation, throughfall and stemflow, respectively. The differences between beech and spruce were rather small compared to the seasonal differences in precipitation isotopes. Isotopic offsets between precipitation and throughfall/stemflow were smaller during the spring and summer months (March through August) than during fall and winter (September through February). Bulk and mobile soil waters at 10 and 40 cm showed smaller seasonal variations than those in precipitation, throughfall and stemflow, and were isotopically lighter than recent precipitation, with the largest offsets occurring during the summer months (June through August) for bulk soil waters. Thus, bulk soil waters at both depths contain a mixture of precipitation from previous events and seasons, with over-representation of isotopically lighter winter precipitation. Mobile soil waters were more similar to recent precipitation than bulk soil waters were. Throughfall isotopes were slightly heavier than precipitation isotopes, resulting in different sinusoidal fits for seasonal isotopic cycles in precipitation and throughfall. These differences lead to small underestimates in the fraction of soil water originating from winter precipitation, when open-field precipitation rather than throughfall is used as the input data. Together our results highlight the importance of isotope measurements in throughfall and stemflow for the assessment of precipitation seasonality and water cycling across forested landscapes.

1 | INTRODUCTION

One third of Switzerland and 40% of the global ice-free land mass are covered by forests (Waring & Running, 2007). Forests alter the amount and chemical composition of water inputs to the underlying soils by retention and evaporation in canopies, understory and litter, accounting for 20% to 40% of annual precipitation (Allen et al., 2017; Floriancic et al., 2022). In forests, precipitation typically reaches the soil as throughfall, precipitation that may or may not have come into contact with the tree, and as stemflow, water that drips along the tree stems (Levia et al., 2011). Canopy interception greatly alters the amount of precipitation reaching forest soils. Thus, forest water interception and retention processes are of great importance to the global freshwater cycle. However, details of this precipitation redistribution remain poorly understood (Allen et al., 2017). Moreover, forest canopies not only modulate the amount of incoming precipitation, but also change the chemical composition and isotopic signals in precipitation (Allen et al., 2015; Dawson et al., 2003). The chemical composition of throughfall and stemflow is further altered upon infiltration into the underlying soils, through mixing with stored soil waters and evaporation from the soil (Benettin et al., 2018; Goldsmith et al., 2018; Pinos et al., 2023).

Naturally, abundant stable water isotopes are an important tool for studying water transport along the soil-plant-atmosphere continuum (Sprenger et al., 2019). Precipitation isotopes are widely used to assess water flow through the subsurface (Sprenger et al., 2016) or plant water uptake (Brinkmann et al., 2019; Rothfuss and Javaux, 2017). However, in forests, isotopic signals in precipitation might be affected by evaporative fractionation, isotopic exchange and mixing processes during redistribution by forest canopies (Allen et al., 2017; Dawson et al., 2003). While throughfall amounts are well correlated to canopy structure, the isotopic composition of throughfall is not (Hsueh et al., 2016); thus, other, temporally varying controls are more important. Previous studies found that the isotopic offset between precipitation, throughfall and stemflow varies between seasons (Pinos et al., 2022) and also varies with rainfall characteristics, such as rainfall amount (Allen et al., 2015), duration (Liu et al., 2008), intensity (Dewalle & Swistock, 1994), and drop size (Pinos et al., 2020). While throughfall offsets have been widely reported, stemflow offsets have been less investigated (Allen et al., 2020; Pinos et al., 2022). This is most likely due to the fact that stemflow typically occurs in small volumes (<2% of total incoming precipitation); nevertheless it can still contribute water and nutrients to the subsurface around tree stems (Carlyle-Moses & Gash, 2011; Snelgrove et al., 2020). Although the change of the isotopic composition in precipitation as it becomes throughfall and stemflow has large effects on the soil water isotopic composition (Klaus & McDonnell, 2013), few studies have directly observed how these offsets between precipitation, throughfall and stemflow affect the composition of soil waters across different seasons. Thus, in this manuscript we quantify the change in isotopic signals when precipitation becomes throughfall and stemflow across different seasons and for different precipitation amounts, and we assess how isotopic offsets from precipitation to throughfall and stemflow affect soil water signatures and their interpretation.

While the differences in isotopic composition between precipitation and throughfall/stemflow have been studied for single events across space (Goldsmith et al., 2018) or different seasons and rainfall intensities (Allen et al., 2015; Pinos et al., 2020; Pinos et al., 2022), assessments of the importance of spatial versus temporal isotopic differences in throughfall and soil waters are rare. Thus, here we compare the temporal variability to the spatial variability to evaluate to which extent spatial and temporal variabilities dominate.

Furthermore, the implications of offsets from precipitation to throughfall and stemflow for assessments of the seasonality in source waters (i.e., soil waters) are not yet well investigated. Evaporative fractionation, mixing processes and tree phenology (i.e., dormant or growing season) might lead to seasonal differences in the extent to which input precipitation changes when dripping through canopies or draining along tree stems (Pinos et al., 2022). Such temporally variable alterations of the isotopic signal of input precipitation might affect our assessments of seasonality and water ages in forest soils, plants, and streamflow. The effects of the isotopic difference between precipitation and throughfall on streamflow water ages were investigated in previous studies, however to our knowledge this has not been investigated for stemflow yet. Stockinger et al. (2015) found that transit times in streamflow were shorter when calculated from throughfall compared to precipitation; on the other hand, Kubota and Tsuboyama (2003) found up to 10% more "old" water in streamflow when estimated from throughfall compared to precipitation. However, assessments of how isotopic differences between precipitation, throughfall and stemflow might affect the inferred seasonal origins of soil waters are rare. The fraction of winter precipitation can be estimated from sinusoidal fits to precipitation and throughfall isotope time series (Jasechko et al., 2014), and similar approaches have been widely used to infer the seasonal origins of waters in streamflow, soils and plant xylem (Allen, Kirchner, et al., 2019; Allen, von Freyberg, et al., 2019; Goldsmith et al., 2022; Jasechko et al., 2017). Thus, here we assess how isotopic changes in throughfall and stemflow may affect inferences about the fraction of winter precipitation in bulk and mobile soil water.

We use a two-year isotope data set of precipitation, throughfall, stemflow, and mobile and bulk soil waters at 10 and 40 cm depth collected in a mixed forest in Switzerland, dominated by beech and spruce, to answer the following research questions:

- By how much do throughfall and stemflow differ isotopically from incoming precipitation?
- Are isotopic differences between precipitation, throughfall and stemflow systematic across seasons and do these differences also affect the bulk soil water isotopic composition?
- To which extent do isotopic offsets between precipitation, throughfall and stemflow affect the estimation of winter precipitation fractions in forest soils?

2 | STUDY SITE AND METHODS

2.1 | The field site and measurement setup

Our analysis is based on data collected at our experimental field site (WaldLab Forest Experimental Site), a small 0.3 km^2 catchment along a mixed forested hillslope dominated by spruce (*Picea abies*) and beech (*Fagus sylvatica*) trees, with a small creek at the bottom, embedded in the larger "Waldlabor Zürich" close to the city of Zurich, Switzerland. The mean annual temperature is 9.3 °C and means annual precipitation is 1134 mm (2000–2022). The soil is a luvisol of approximately 100 cm depth, on top of ~6 m moraine material from the last glacial maximum. The dominant soil structure is silty sand, with clay fractions below 10%.

Since March 2020 we have measured major climate parameters (i.e., precipitation amount, temperature, vapour pressure deficit, wind speed etc.) on grassland approximately 150 m outside the forest at 1.5 m height with a compact all-in-one weather station (Meter AG – Atmos 41) at 10-min resolution. At the same location, we also collected precipitation samples for isotope analysis with a funnel draining into a glass bottle through a syringe to avoid evaporation as described in von Freyberg et al. (2020). Throughfall gutters (below one beech canopy, one spruce canopy and multiple young spruce canopies) and stemflow collectors (on one beech and one spruce tree) fed into Davis (Rain Collector II) tipping buckets, and samples were collected below into glass bottles. All bottles were emptied after each event larger 3 mm, typically on the same day or the morning of the next day. For the observation period (01 April 2020 through 31 March 2022), we collected a total of 175 precipitation samples from events with a mean intensity of 12.1 mm d^{-1}. Only 5 out of the 175 precipitation events in the observation period were snowfall events. From throughfall, we collected 170 samples below beech, 170 samples below spruce and 167 samples below young spruce canopies. From stemflow, we collected 161 samples for beech and 142 samples for spruce.

We sampled mobile soil water (the fraction of soil water that has no direct surface contact with the soil, thus is held cohesively and can move freely) and bulk soil water (including also the fraction of soil water that is stored in hydration spheres of clay minerals, held tightly inside the capillary spaces). Mobile soil water (SW_{mobile}) was sampled twice per week at 10 and 40 cm depth at two sites (Figure 1) with suction lysimeters (Slim Tube Soil Water Sampler, Soil Moisture Equipment Corp). We applied a suction of 0.7 bar on Mondays and sampled the water on Thursdays; we then applied suction again and emptied the samplers again on the following Mondays. For the observation period (01 April 2020 through 31 March 2022), we collected a total of 140 mobile soil water samples at 10 cm depth and 166 mobile soil water samples at 40 cm depth. In addition, we sampled bulk soil (SW_{bulk}) at two locations (Figure 1) in 10 and 40 cm depth with a 2 cm wide auger, roughly every 3 weeks from the beginning of July 2020 through end of March 2022, and extracted the water cryogenically. We collected a total of 132 bulk soil water samples at 10 cm depth and 126 bulk soil water samples at 40 cm depth. We selected these two sampling depths for mobile and bulk soil waters because 10 cm depth is expected to reflect the isotopic composition in the top soil and 40 cm depth is around the main water uptake depth of beech and spruce trees at our site (Floriancic et al., 2023; Martinetti et al., 2023).

2.2 | Isotope analysis, and evaluation

Bulk soil samples were stored in exetainers (12 mL Exetainer, Labco Ltd., Ceredigion, UK) at −18 °C until extraction. Cryogenic water extraction was performed at ETH Zurich (Grassland Science Group). The samples were evaporated in a water bath at a temperature of 80 °C for 3 h with a suction of 10^{-2} MPa, the water was collected in *u*-shaped tubes immersed in liquid nitrogen (Sun et al., 2022). We did not check for the extraction efficiency explicitly in this study, however, in a previous study by Bernhard et al. (2023) we could show that for all samples extraction efficiencies exceeded 95%. Extracted samples, along with samples of precipitation, throughfall and stemflow, were stored in 1.5 mL glass vials (BGB Analytik, Boeckten, Switzerland) and refrigerated at 2 °C until analysis. The isotopic

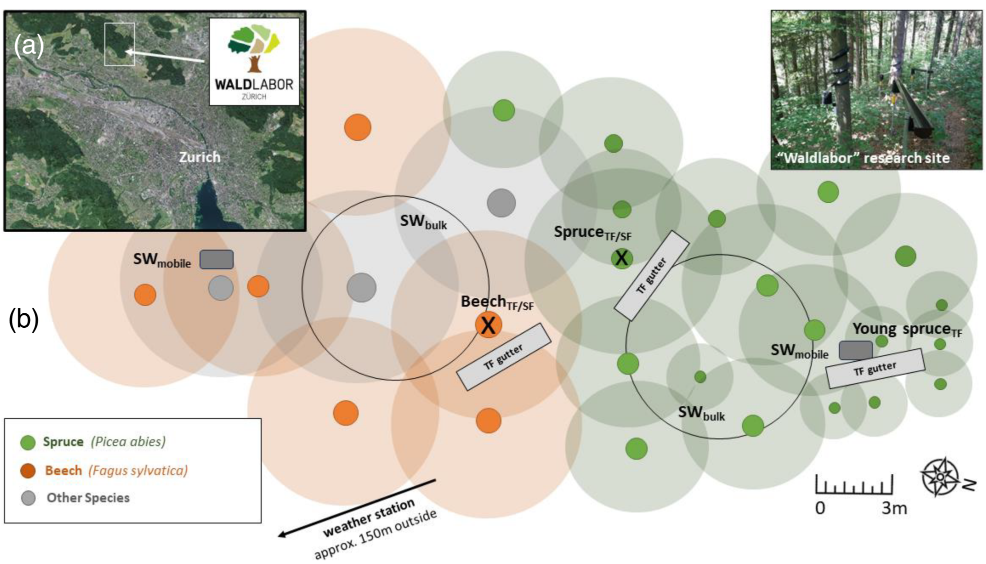

FIGURE 1 Location of the 'Waldlabor' in Zurich (a) and a schematic of our 'WaldLab Forest Experimental Site' (b), indicating the locations of trees (spruce, beech and other species shown in green, orange and grey), the trees where throughfall (TF gutter, indicated by light grey boxes) and stemflow (SF) were measured, and the locations of bulk soil sampling (SW_{bulk}, indicated by the black circles) and mobile soil sampling (SW_{mobile}, indicated by the dark grey boxes). The weather station and precipitation collector are located outside the forest, in an open field approximately 150 m from our experimental site.

composition was analysed with a triple isotope water analyser (Los Gatos – TIWA-45-EP) with a precision of <1 ‰ for ^{2}H and <0.2 ‰ for ^{18}O, as determined by long-term replicate sampling of standards.

We present the isotope data in time series in per mil (‰) notation (Kendall & Caldwell, 1998) relative to V-SMOW (Vienna Standard Mean Ocean Water). Data of δ^{2}H are shown throughout this paper; the corresponding δ^{18}O data can be found in the supplement, as well as in our dual-isotope plots. The regression lines in the dual-isotope plots are calculated by reduced major axis regression (described in Harper, 2016) instead of linear regression. Classic linear regression assumes that the x-axis has no error/uncertainty, but a dual-isotope plot has uncertainty on both axes, making reduced major axis regression a more appropriate method.

To focus specifically on evaporation effects among throughfall, stemflow and soil samples relative to precipitation, we also calculated the line-conditioned excess (LC-excess) as the deviation from the LMWL for each sample following Landwehr and Coplen (2004). Note that the LMWL was also fitted by reduced major axis regression,

$$\mathrm{LC-excess} = \delta^{2}H_{x} - a_{LMWL}\, x\, \delta^{18}O_{x} - b_{LMWL}$$

where the LMWL is

$$\delta^{2}\mathrm{H} = 7.96 \times \delta^{18}\mathrm{O} + 11.70$$

In seasonal climates, the stable isotope ratios of water (^{18}O/^{16}O and ^{2}H/^{1}H) in precipitation differ between summer and winter. Typically, precipitation in continental interiors is isotopically heavier in summer than in winter, resulting in a seasonal cycle of precipitation isotopic signatures. This seasonal cycle of precipitation isotopes can be used to assess the seasonal origin of waters found in soils, streamflow or xylem. Here we used seasonal cycles in precipitation (and throughfall) isotopes to assess the fraction of winter precipitation in bulk and mobile soil waters, following the method described in Jasechko et al. (2014). Robust sinusoidal fits to the seasonal cycles of precipitation (and throughfall) were obtained using iteratively re-weighted least squares (IRLS), based on an *R* script in the supplement of von Freyberg et al. (2018). We used the minima and maxima (or peaks) of these fitted seasonal cycles as winter and summer end-members in calculating the fractions of winter precipitation found in bulk and mobile soil waters, as suggested in Jasechko et al. (2014).

Wilcoxon signed rank tests were used to compare the means of two independent samples, with $p < 0.05$ used to infer that the tested datasets are not similar to each other.

3 | RESULTS & DISCUSSION

3.1 | Isotopic variation of precipitation, throughfall, stemflow and bulk soil waters

Timeseries of precipitation, throughfall and stemflow did contain the expected typical seasonal cycle of lighter isotopic signatures during the winter months and heavier isotopic signatures during the summer months (Figure 2). The mean isotope ratios were −64.3 ‰ and −9.6 ‰ for δ^{2}H and δ^{18}O, respectively, in precipitation, −59.9 ‰ and −9.5 ‰ in throughfall, and −56.3 ‰ and −8.8 ‰ in stemflow. The δ^{2}H compositions of precipitation, throughfall, and stemflow averaged −78.8, −74.1, and −68.3 ‰ respectively, in the winter half of the year (November through April), and −52.5, −48.0, and −45.7 ‰, respectively, in the summer half of the year (May through October); the corresponding values for δ^{18}O were −11.6, −11.6, and −7.7 ‰ for precipitation, throughfall, and stemflow in the summer half of the year, and −7.8, −7.7, and −7.2 ‰ in the winter half of the year. Thus, the seasonal variations in precipitation, throughfall, and stemflow were typically much larger than the isotopic offsets between them, particularly for δ^{2}H. Differences in throughfall and stemflow isotopic signatures between species were small and not statistically significant (Table 1). Mean bulk soil water isotopic signatures varied from −74.7 to −82.2 ‰ (−10.3 to −11.8 ‰ for δ^{18}O) at 10 and 40 cm depth, respectively. Differences between summer and winter were considerably larger at 10 cm depth compared to 40 cm depth (Table 1). Bulk soil waters were in general isotopically lighter than precipitation, throughfall and stemflow, and became isotopically lighter from 10 to 40 cm depth. Mean mobile soil water isotopic signatures varied from −61.4% to −67.0 ‰ (−9.0% to −10.0 ‰ for δ^{18}O) at 10 and 40 cm depth, respectively. Isotopic differences between summer and winter mobile waters were considerably larger at 10 cm depth compared to 40 cm depth. Mobile soil water was isotopically heavier than bulk soil water and closer to precipitation, throughfall and stemflow.

3.2 | Offsets between incoming precipitation, throughfall, stemflow and soil waters

In Figure 3 we compare the δ^{2}H isotopic composition in throughfall, stemflow, bulk soil water and mobile soil water to δ^{2}H in recent precipitation. For throughfall and stemflow, precipitation during the same event serves as the reference, whereas mobile and bulk soil waters are compared to the volume-weighted average composition of all precipitation that fell since the previous soil water sample was collected. While throughfall from beech, spruce and young spruce was isotopically only slightly heavier than precipitation, stemflow was distinctly enriched in heavy isotopes, as indicated by the reduced major axis regression lines lying farther above the one-to-one line. Throughfall and precipitation were isotopically not significantly different from each other (paired Wilcoxon Rank test; $p > 0.05$), while stemflow isotopic signatures were significantly different from precipitation isotopic signatures for both beech and spruce ($p < 0.05$).

Bulk soil water signatures were typically lighter than recent precipitation, indicated by the majority of points lying below the one-to-one line. Isotopically lighter soil waters were evident in bulk soils in 10 cm depth, but even more evident for samples in 40 cm depth. Differences in the isotopic signatures of bulk soil waters and recent precipitation were significant (Wilcoxon Signed Rank test, $p < 0.05$) for both 10 and 40 cm depth. The majority of mobile soil water was

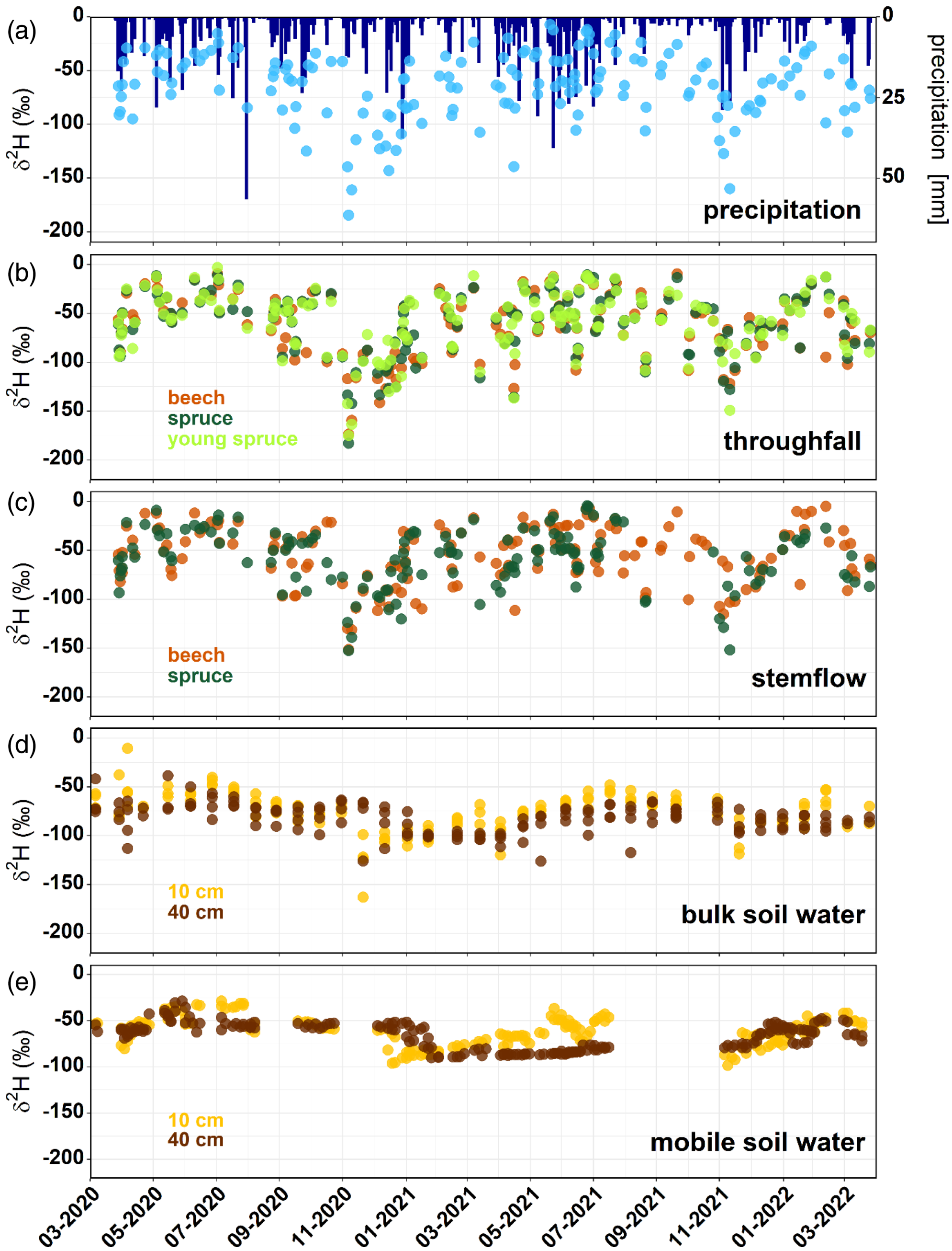

FIGURE 2 Timeseries of water fluxes and δ^2H isotopic composition in precipitation (a), δ^2H in throughfall (b), δ^2H in stemflow (c) measured at two different species (beech and spruce), and δ^2H in bulk (d) and mobile (e) soil waters at 10 and 40 cm depth from April 2020 through April 2022. Similar results are shown for $\delta^{18}O$ in supplementary material Figure S1.

TABLE 1 Isotopic signatures in precipitation, throughfall, stemflow and bulk and mobile soil waters at 10 and 40 cm depth for the whole observation period, and for the winter (November through April) and summer (May through October) halves of the year.

	Precipitation		Throughfall beech		Throughfall spruce		Throughfall young spruce		Stemflow beech	
	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$
Mean	−64.3	−9.6	−60.8	−9.4	−59.7	−9.6	−59.2	−9.5	−54.5	−8.6
Winter	−78.7	−11.6	−76.0	−11.6	−74.0	−11.6	−72.4	−11.4	−65.7	−10.4
Summer	−52.5	−7.8	−48.3	−7.6	−47.2	−7.8	−48.4	−7.9	−45.0	−7.1
	Bulk soil 10 cm		**Bulk soil 40 cm**		**Mobile soil 10 cm**		**Mobile Soil 40 cm**		**Stemflow spruce**	
	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$
Mean	−74.7	−10.3	−82.2	−11.8	−61.4	−9.0	−67.0	−10.0	−58.0	−9.0
Winter	−85.1	−11.6	−85.5	−12.4	−69.1	−10.2	−71.1	−10.7	−71.0	−11.0
Summer	−64.9	−9.1	−79.2	−11.3	−53.6	−7.7	−61.7	−9.1	−46.5	−7.2

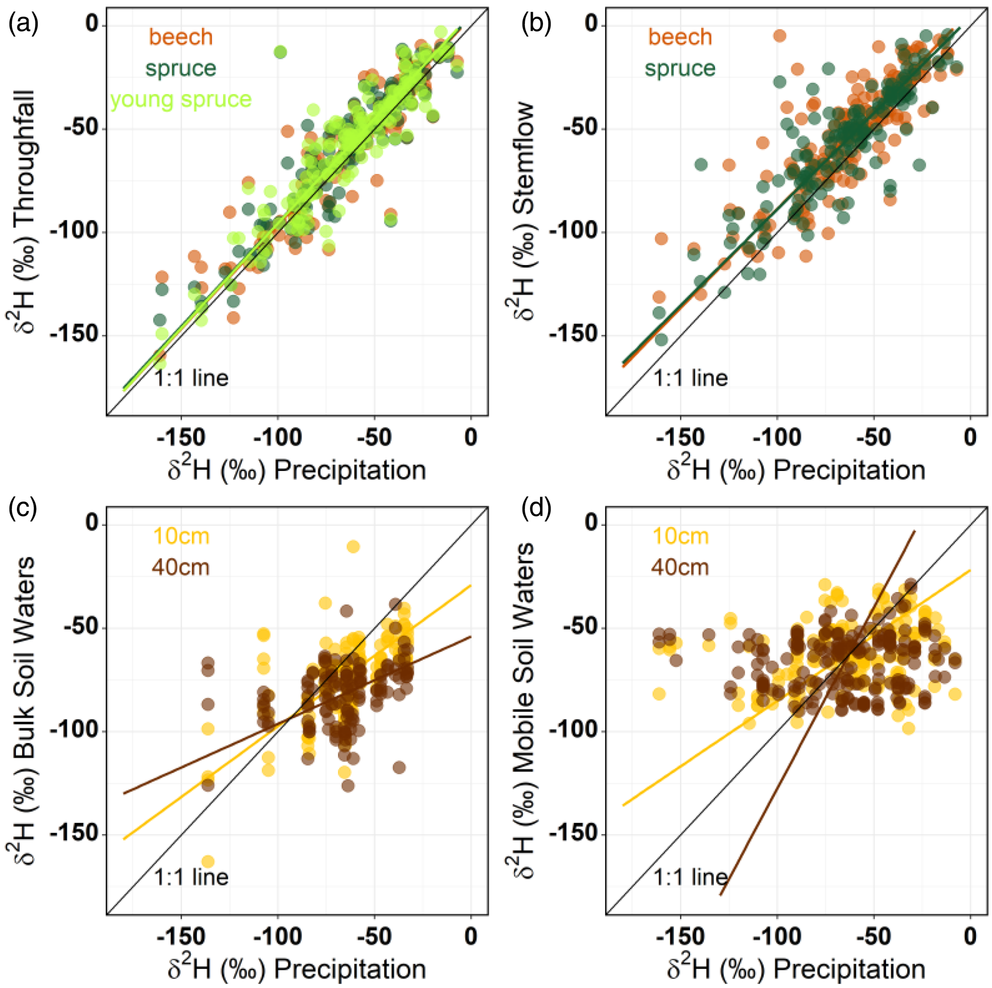

FIGURE 3 The ratio of δ^2H isotopic composition measured in precipitation and throughfall (a), in precipitation and stemflow (b) and precipitation and soil waters of 10 and 40 cm depth, respectively. The black line indicates the 1:1 line, the coloured lines indicate the Reduced Major Axis regression lines. Similar results for δ^{18}O are shown in supplementary material Figure S2.

isotopically lighter than recent precipitation, indicated by the majority of points lying below the one-to-one line. Mobile soil waters at 10 and 40 cm depth were significantly different from each other but on average not significantly different from recent precipitation (Wilcoxon Signed Rank test, $p > 0.05$). However, the distributions of isotopic signatures in mobile soil waters at 10 and 40 cm depth were different than the distribution of isotopic signatures in recent precipitation (Kolmogorov–Smirnov two-sample test, $p < 0.05$).

When precipitation becomes throughfall and stemflow, typically three factors lead to offsets in the isotopic signals: evaporation, liquid–vapour exchanges and selection through routing processes in the canopy (Allen et al., 2017). At our study site, differences between the isotopic compositions measured in precipitation, throughfall and stemflow were small overall; inter-species differences in throughfall and stemflow were also small. In 17 out of 22 throughfall isotope studies reviewed by Allen et al. (2017), throughfall isotopes were heavier than incoming precipitation, with average differences of 0.19 ‰ in δ^{18}O, and Pinos et al. (2022) found an average offset of 0.3 ‰ in δ^{18}O. The mean offsets of δ^{18}O and δ^2H isotopes between precipitation and throughfall in our dataset were 0.1 ‰ and 4.5 ‰, respectively. However, offsets can be larger for individual events, including events in which throughfall is isotopically lighter than incoming precipitation, both at our site and in the studies reviewed by Allen et al. (2017). Previous studies have shown that isotopic offsets for coniferous species are typically larger than isotopic offsets in throughfall below broadleaf species (e.g., Brodersen et al., 2000; Dewalle & Swistock, 1994; Xu et al., 2014) due to the larger storage capacity of conifer canopies. This is generally consistent with findings at our site for δ^2H, where the mean offsets between precipitation and spruce and young spruce throughfall (4.7 ‰ and 5.2 ‰, respectively) were larger than the offset below beech (3.6 ‰), with a standard error of 0.2 ‰ for all three species.

Although evaporative fractionation effects would lead to heavier isotopes in throughfall (and stemflow), our dataset's overall slightly heavier isotopic signals in throughfall (and stemflow) can most likely be attributed to selection and exchange with antecedent vapour occurring in the canopies or along the stem (Allen et al., 2017; Gat & Tzur, 1967). However, to fully clarify the mechanisms involved, further data at high temporal resolution and research on intra-event variations in the isotopic composition of precipitation, throughfall and stemflow are warranted.

Bulk soil water was isotopically lighter at 40 cm depth than at 10 cm depth, and typically lighter than precipitation at both depths. This is expected because evapotranspiration losses imply that precipitation and throughfall will be less likely to infiltrate to deeper soil layers during summer (Goldsmith et al., 2018; Sprenger et al., 2017). This inference is also supported by the differences between winter and summer bulk and mobile soil water signatures, which were larger at 10 cm depth than at 40 cm depth, driven by the seasonal isotopic fluctuations from recent precipitation (i.e., the average difference in δ^2H between winter and summer was 20.1 ‰ and 6.3 ‰ for 10 and 40 cm, respectively, for bulk soil waters and 15.5 ‰ and 9.5 ‰, respectively, for mobile soil waters). Overall, bulk soil waters (at 10 cm but even more at 40 cm) showed a bias towards isotopically lighter (most likely winter) precipitation stored in the soil, rather than resembling more recent precipitation, whereas mobile soil waters were closer to recent precipitation.

3.3 | Seasonal isotopic offsets between precipitation, throughfall, stemflow and soil waters

Deviations of the isotopic composition in throughfall, stemflow and bulk soil waters compared to precipitation were different across the four seasons (Figure 4). While in September through November (called SON below) throughfall and stemflow were more similar to recent precipitation, differences were larger during the spring months (March through May, called MAM below) and most variable during the winter months (December through February, called DJF below). Seasonal differences between the deviations of precipitation and throughfall and precipitation and stemflow were not significant (Wilcoxon Signed Rank test, p-value >0.05), with the exception for stemflow of beech trees in MAM (Figure 4b). Throughfall was typically heavier compared to stemflow, however differences were non-significant (Figure 4c). The offsets between precipitation, throughfall and stemflow were not strongly related to climate variables like mean daily temperature or VPD (Spearman rank correlations between offset and climate variables were <0.1). We also calculated the offset between precipitation, throughfall and stemflow isotopes for the 25% of events with lowest precipitation and for the 25% of events with highest precipitation and found small and largely non-significant differences (results were significant only for beech throughfall in June through August, called JJA below). Thus, the amount of incoming precipitation has only a minor effect on the isotopic offsets between precipitation, throughfall and stemflow.

Bulk soil water signals at 10 cm depth were significantly different between all four seasons (MAM, JJA, SON, DJF; Figure 4d). At 40 cm depth, bulk soil water signals were not significantly different only between SON and JJA and MAM and DJF (Wilcoxon Signed Rank test, p-value >0.05). Mobile soil water signals at 10 cm were significantly different between all four seasons (MAM, JJA, SON, DJF; Figure 4e), except for SON and MAM. Mobile soil water signals in 40 cm were significantly different for all four seasons, except for SON and JJA (Wilcoxon Signed Rank test, p-value >0.05). We also calculated the offset between precipitation and bulk and mobile soil water isotopes at 10 and 40 cm depth for the 25% of events with lowest precipitation and for the 25% of events with highest precipitation and found small and largely non-significant differences (results were significant only for bulk soil at 10 cm depth in DJF).

Previous studies found that the isotopic offsets between precipitation, throughfall and stemflow vary between seasons and with rainfall characteristics (Allen et al., 2015; Dewalle & Swistock, 1994; Liu et al., 2008; Pinos et al., 2020; Pinos et al., 2022). At our site, we observed small, non-significant, differences in offsets between the lower and upper quartiles of rainfall amount (Figure 4). Several studies report that for smaller precipitation events, throughfall is likely to be lighter than precipitation (Allen et al., 2017), which is only the case for a few events at our study site, indicated by the medians of throughfall isotopic weight being heavier for all species (Figure 4a). Pinos et al. (2022) and Snelgrove et al. (2020) also did not find significant relations between the amount and intensity of precipitation and the change in isotopic signatures in throughfall and stemflow.

Although stemflow water fluxes are typically small (<2% of precipitation), they are highly enriched with nutrients and affect subsurface water availability and isotopic signatures around the stem (Carlyle-Moses & Gash, 2011; Snelgrove et al., 2020). At our site stemflow was typically heavier than precipitation and throughfall, which is consistent with previous studies (Brodersen et al., 2000; Cayuela et al., 2018; Pinos et al., 2022). Average isotopic offsets from precipitation δ^{18}O in throughfall and stemflow at our site (0.1 ‰ and 0.8 ‰, respectively) were slightly smaller than those found by Pinos et al. (2022) of 0.3 ‰ and 1.1 ‰. However, we found substantial seasonal variation in these offsets, with maxima of 0.4 ‰ and 1.0 ‰ in JJA for throughfall and stemflow, respectively. The higher isotopic weight of stemflow compared to throughfall (and precipitation) can be attributed to longer flow paths (Klamerus-Iwan et al., 2020; Levia et al., 2011) and thus longer exposure to evaporation, exchange and selection (Allen et al., 2017; Ikawa et al., 2011).

Previous studies found larger offsets below denser canopies, with throughfall being heavier than precipitation (e.g., Dewalle & Swistock, 1994; Liu et al., 2008), which is not surprising, as dense canopies also have larger storage capacity (Carlyle-Moses & Gash, 2011). This is the case for our site, where canopy cover and isotopic offsets are highest in JJA and SON below beech, followed by spruce and young spruce (Grundmann et al., 2023). This is also consistent with the findings of Cayuela et al. (2018) and Pinos et al. (2022), who also found larger enrichment of stemflow during the main growing season. However, both studies reported that enrichment in throughfall was larger during the dormant season, potentially caused by the dominance of convective storms with short duration but high intensity during the main growing season (Pinos et al., 2020).

The isotopic offset between precipitation and soil waters at our site was largest during the summer months (JJA), where one would expect evaporative enrichment and precipitation from isotopically heavier summer events mixing with waters stored in the soil from previous isotopically lighter events (Sprenger et al., 2016). The offset was larger at 40 cm depth compared to 10 cm depth. The largest differences between the δ^2H isotopic signals at 10 and 40 cm was found in January and March (consistent with findings in Sprenger et al., 2017), as well as in April, September and November, that is, mainly outside

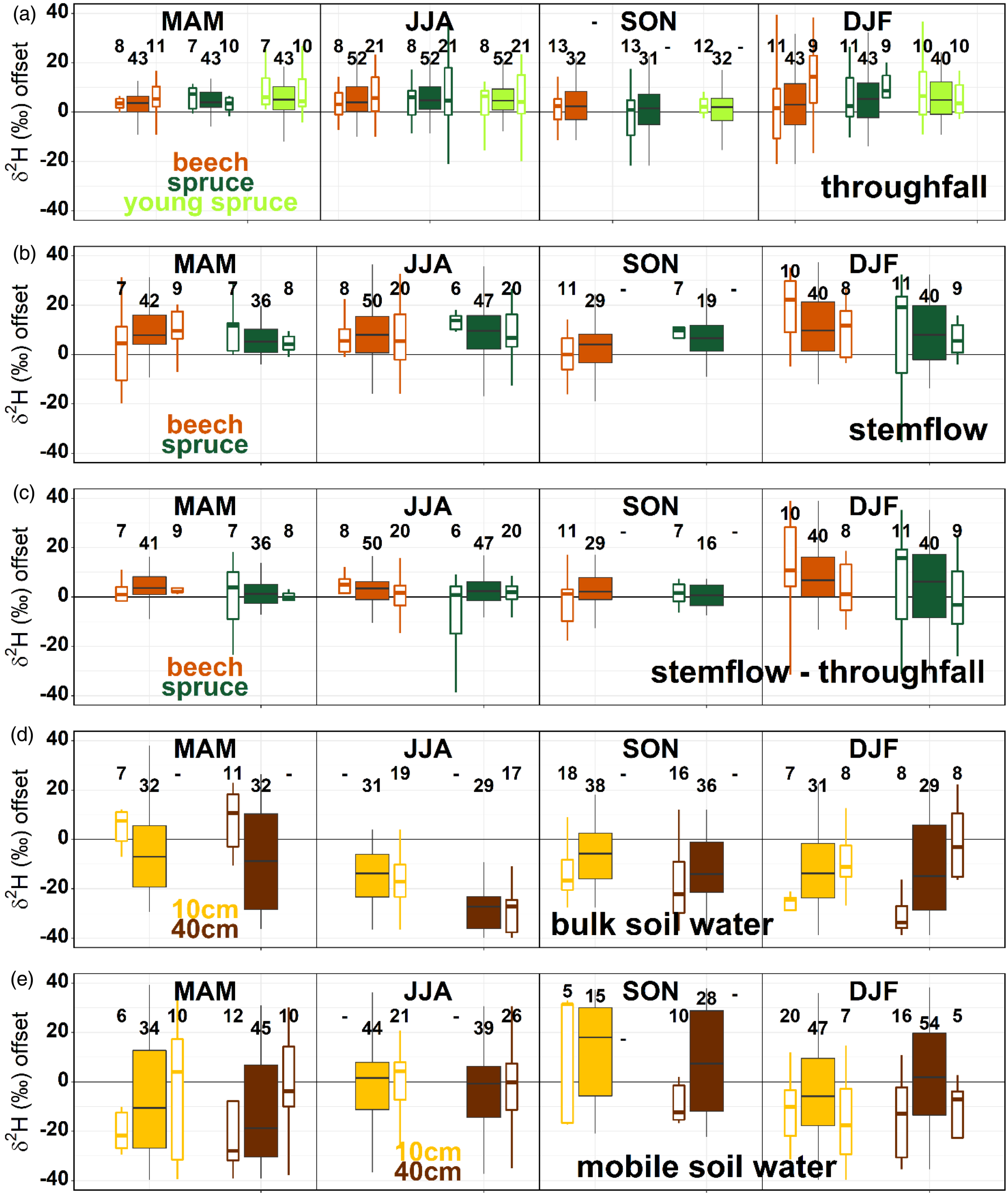

FIGURE 4 The deviation of the isotopic δ^2H signal in throughfall for beech, spruce and young spruce (a), stemflow of beech and spruce (b) and bulk soil waters at 10 and 40 cm depth (c) from the δ^2H signal in precipitation for the different seasons (MAM – March through May, JJA – June through August, SON – September through November, DJF – December through February), for the entire dataset (larger coloured boxplots) and the lower and upper quartiles of precipitation (hollow boxplots on the left and right sides, respectively). Subpanel d shows the difference between throughfall and stemflow for beech and spruce. The numbers on top of each boxplot indicate the number of samples. Please note that there were too few low or high magnitude precipitation events for some of the seasons. Similar results are shown in the supplementary material Figure S3 for ^{18}O.

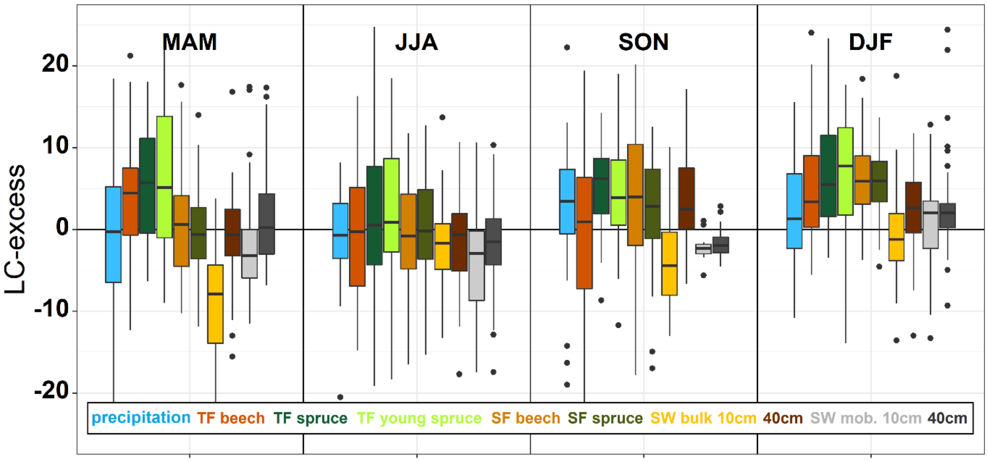

FIGURE 5 LC-excess of precipitation, throughfall (below beech, spruce and young spruce canopies), stemflow (from beech and spruce trees) and bulk and mobile soil waters at 10 and 40 cm depths for the four seasons MAM, JJA, SON and DJF.

of the growing season. This is consistent with water uptake of trees leading to a homogenization of the soil isotopic signal, mainly due to shallower soil waters that can fill up empty pore space in deeper layers when water is removed by tree water uptake. For example, in Martinetti et al. (2023) we found evidence for hydraulic lift at our study site that potentially also leads to a homogenization of the isotopic signal. This might be reflected in the smaller differences found between soil water isotopes at 10 and 40 cm depth from May through August.

We further calculated the line conditioned excess for precipitation, throughfall, stemflow and bulk soil waters (Figure 5) for all four seasons (MAM, JJA, SON; DJF). Mean LC-excess for throughfall was 2.08 (with a standard deviation of ±7.80), 4.76 (± 7.45) and 4.55 (± 8.22) for beech, spruce and young spruce, respectively. Mean LC-excess for stemflow was 2.31 (± 7.40) and 1.86 (± 6.43) for beech and spruce, respectively. However, LC-excess varied seasonally, being more positive for throughfall and stemflow during SON and even more positive for DJF, while throughfall and stemflow were closer to the local meteoric water line across the spring and summer months (MAM and JJA). We found significant differences in throughfall LC-excess between beech and both spruce and young spruce but not in stemflow between beech and spruce (Wilcoxon Signed Rank test, *p*-value >0.05).

LC-excess values in bulk soil waters at 10 and 40 cm depths were significantly different from each other. Bulk soil waters at 10 cm depth were close to the local meteoric water line from December through February as well as in JJA, but LC-excess was negative for SON and MAM, with an annual mean of −4.71 (with a standard deviation of ±7.34). Bulk soil waters of 40 cm depth were close to the local meteoric water line in MAM, JJA and DJF and more positive in SON, with an annual mean of −0.74 (± 8.55). LC-excess in mobile soil waters at 10 and 40 cm depth were not significantly different from each other. Mobile soil waters at 10 cm depth were close to the local meteoric water line for DJF and slightly negative for MAM, JJA and SON, with an annual mean of 0.26 (± 8.14). Bulk soil waters at 40 cm depth were close to the local meteoric water line in MAM, JJA and DJF, with an annual mean of −1.74 (± 6.08).

3.4 | Spatial versus temporal isotopic variation of throughfall and soil waters

Many previous studies indicate that the spatial variation of throughfall and stemflow for a single event can be larger than the mean offset between precipitation, throughfall and stemflow (Allen et al., 2017). We calculated the median absolute deviation (MAD) for throughfall and stemflow for the entire two-year period and for the difference between species (beech, spruce and young spruce for throughfall, and beech and spruce for stemflow). The temporal variability of the isotopic signatures in throughfall (MAD of >28 ‰ across the entire two-year dataset) was much larger than the spatial variability between the three throughfall plots (median absolute deviation of 3.3 ‰ between same-day samples, across all pairs among the three throughfall plots). These results are consistent with the findings of Goldsmith et al. (2018), who found MAD of 2.5 ‰ in throughfall during a single event at 142 measurement locations across a 100 × 100 m plot. Similarly, the temporal variability of the isotopic signatures in stemflow (MAD of >29 ‰ across the entire two-year dataset) was much larger than the spatial variability between the two stemflow plots (median absolute deviation of 6.6 ‰ between same-day samples in the two stemflow plots). The spatial variation in throughfall (and stemflow) tends to be much smaller than the overall seasonal variability. This indicates that the change of the isotopic signal through canopy processes and alteration of the throughfall signal by evaporation, exchange and selection in seasonal climates as in Switzerland is much smaller than the seasonal variation of incoming precipitation. Differences in throughfall and stemflow at a single site are commonly observed (see Allen et al., 2017 for a review) however, while spatial variability in throughfall exists across our site and the site of Goldsmith et al. (2018), the much greater temporal variability in throughfall implies that temporally dense sampling (i.e., intra-event sampling) may be more important than extensive spatial replication in future sampling designs. Nevertheless, offsets between precipitation and throughfall exist across space and time, so ignoring them (i.e., by only considering open-field precipitation) can introduce biases in studies of subsurface water movement or plant water uptake across forested landscapes (Klaus & McDonnell, 2013).

We also compared the temporal and spatial variability in bulk and mobile soil waters (typically two sampling sites during each timestep for mobile soil water, and four sampling sites during each timestep for bulk soil water, at each of two depths, 10 and 40 cm). The temporal variability of the isotopic signatures in mobile soil waters (MAD of 16.3 and 13.6 ‰ across the entire two-year dataset at depths of 10 and 40 cm, respectively) was about four times larger than the spatial variability between the four different sampling sites (MAD of 6.3 and 5.2 ‰ between same-day samples from the two mobile soil water samples, at depths of 10 and 40 cm, respectively). The temporal variability of the isotopic signatures in bulk soil waters (MAD of 17.6‰ and 13.6 ‰ across the entire two-year dataset at depths of 10 and 40 cm, respectively) was only about two to three times larger than the spatial variability between same-day samples at the four different sampling sites (MAD of 6.5 and 5.9 ‰ between all pairs of same-day bulk soil water samples, at depths of 10 and 40 cm, respectively). These results are broadly consistent with the MAD of 10.3 and 7.4 ‰, for 10 cm ($n = 149$) and 40 cm ($n = 8$), respectively, of bulk soil waters measured during one sampling campaign by Goldsmith et al. (2018). This indicates that a few spatially distributed samples might not be sufficient to reliably assess water isotopic signatures, especially in shallow soils. Thus, caution is warranted when estimating soil water transport and root water uptake based on only a few sampling locations, as soil water isotopic signatures can be very heterogeneous during a single timestep.

3.5 | Implications of throughfall and stemflow isotopic offsets for the estimation of winter precipitation fractions

We found that the isotopic signal in precipitation was slightly altered in throughfall and stemflow, with small variations across seasons. The open question remains how this change in isotopic signals from precipitation to throughfall and stemflow affects the assessment of seasonal patterns in soils, and thus in the potential receivers of soil waters (such as groundwater recharge, streamflow, and xylem waters). Throughfall isotopes were slightly heavier than precipitation isotopes, resulting in different sinusoidal fits to seasonal variations in precipitation and throughfall (Figure 6). If we estimate the fraction of winter

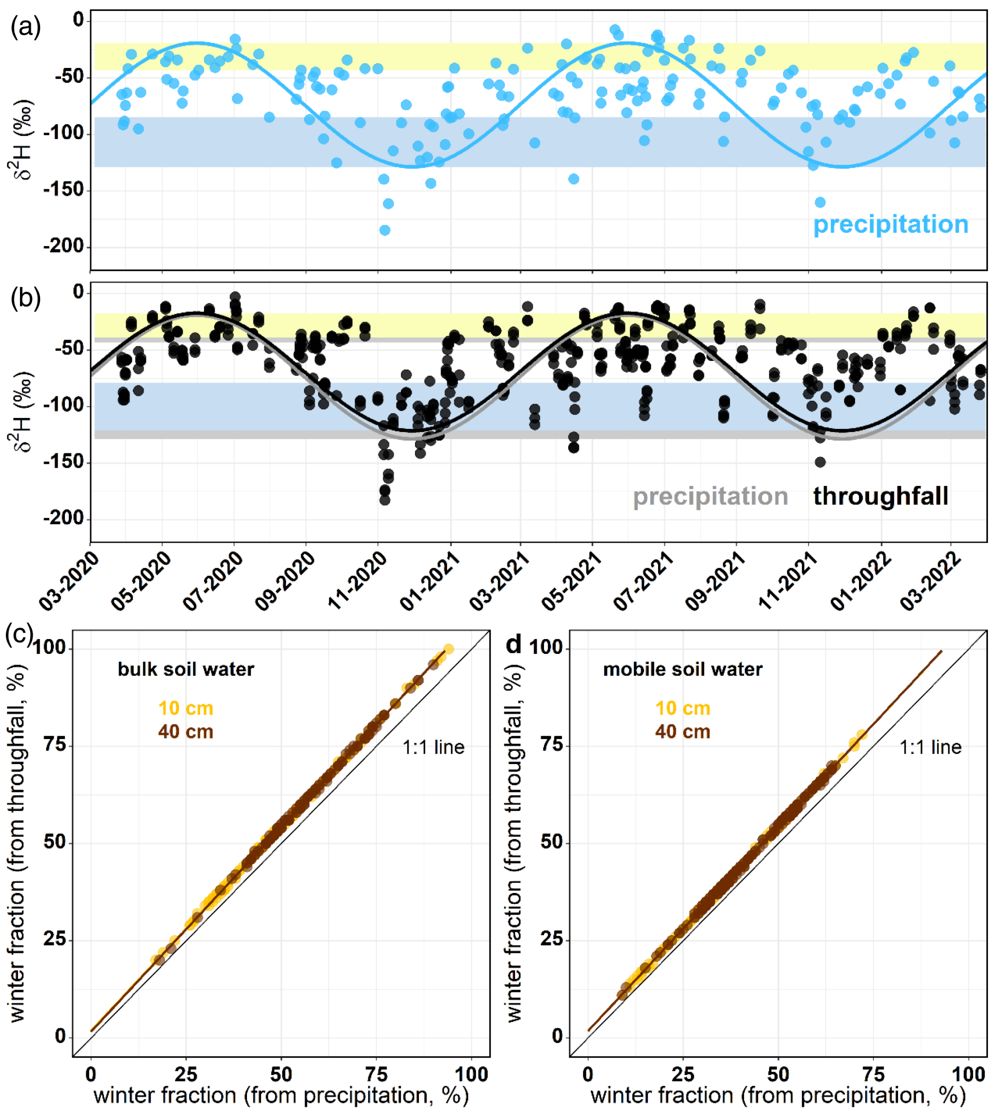

FIGURE 6 Sinusoidal fits for precipitation (a) and throughfall (black) and precipitation (grey) (b). The yellow shading indicates the typical range of summer precipitation (upper quartile); the blue shading indicates the typical range of winter precipitation (lower quartile). Throughfall is systematically heavier compared to precipitation. The fractions of winter precipitation in bulk (c) and mobile (d) soil water are systematically smaller when calculated from open-field precipitation, compared to the winter fractions calculated from throughfall.

water in soils using open-field precipitation rather than throughfall as our input, we underestimate the winter water fraction in bulk and mobile soils by an average of 4.5% and 3.5%, respectively (Figure 6). Average winter fractions for bulk soils were 51% and 57% for 10 and 40 cm depth, respectively, when calculated from the seasonal precipitation isotope cycle and 55% and 62% for 10 and 40 cm depth, respectively, when calculated from the seasonal throughfall isotope cycle. Average winter fractions for mobile soils were 39% and 44% for 10 and 40 cm depth, respectively when calculated from the seasonal precipitation isotope cycle and 42% and 48% for 10 and 40 cm depth, respectively when calculated from the seasonal throughfall isotope cycle. Winter fractions were generally larger in bulk soil waters than in mobile soil waters, and smaller at 10 cm depth than at 40 cm depth.

Interception in canopies and water transport along the stem affect isotopic signatures and are likely affecting our interpretation of water fluxes in the underlying compartments of the forest water cycle (i.e., soil waters, streamflow and plant water uptake). For example, Stockinger et al. (2015) found that transit times in streamflow were shorter when calculated from throughfall compared to precipitation. On the other hand, Kubota and Tsuboyama (2003) found up to 10% more "old" water in streamflow when estimated from throughfall compared to precipitation. Both studies highlight the importance of isotopic measurements of throughfall for correctly assessing water ages in streamflow. However, in our estimates of fractions of winter precipitation in soil waters, the relatively small isotopic offsets between precipitation and throughfall resulted in only a 3.5% to 4.5% bias for winter fractions in mobile and bulk soil water, respectively. This bias is relatively small because the calculation of winter fractions is based on long-term average isotope signatures of the winter and summer seasons (Allen et al., 2017). Inferences drawn from shorter-term isotopic signatures, such as hydrograph separations of individual events, will be more vulnerable to the larger short-term isotopic differences between precipitation, throughfall, and stemflow.

Using precipitation instead of throughfall isotopes may bias assessments of the seasonal origins of plant water uptake or streamflow. Due to the scarcity of throughfall isotope measurements, many previous studies have used open-field precipitation isotope data instead (e.g., Allen, von Freyberg, et al., 2019; Goldsmith et al., 2022) even in forested settings, only a few studies have used throughfall measurements (e.g., Knighton et al., 2019; Magh et al., 2020; Nehemy et al., 2022). Most studies have found that throughfall is isotopically heavier than precipitation (see review by Allen et al., 2017), so calculations based on precipitation rather than throughfall should be expected to typically underestimate the importance of winter precipitation (at least in regions where precipitation is isotopically lighter in winter than in summer). However, at our site (and in the studies of Knighton et al., 2019 and Nehemy et al., 2022), these differences between open field precipitation and throughfall / stemflow were small, implying that the differences in the calculation of winter fractions in soil waters should also be small.

4 | CONCLUSION

At our site, forest canopies did not change the isotopic signals found in precipitation to a large extent; nevertheless, caution is needed when using open-field precipitation to draw inferences about forest water cycling. Typical throughfall and stemflow samples were isotopically heavier than precipitation (Figure 3), potentially due to evaporation, selection processes or exchange with ambient vapour on the way to the forest floor. Stemflow was isotopically heavier, on average, than throughfall (Figure 4c).

Our measurements showed that seasonal isotopic signatures in precipitation, throughfall and stemflow were damped in bulk soils at 10 and 40 cm (Figure 1). Bulk soil waters were significantly different between 10 and 40 cm depths, most likely reflecting different degrees of subsurface mixing with waters from previous events and seasons. Bulk soil waters were typically isotopically lighter than precipitation, throughfall and stemflow (Figure 2), with the largest isotopic differences occurring in summer (Figure 4d), whereas mobile soil waters were more consistent with recent precipitation (Figure 4e).

Isotopic offsets in throughfall and stemflow relative to precipitation differed across seasons (Figure 4), implying that shorter-term studies of throughfall and stemflow isotopes may be unrepresentative of long-term behaviour. Throughfall and stemflow were spatially variable, but seasonal and shorter-term temporal variations across our two-year dataset were much larger. However, in bulk soil waters, temporal variations across our two-year study were only two to three times larger than the spatial variability between sites. Careful sampling design is needed to ensure that soil water end members are adequately constrained in isotopic studies of subsurface transport and plant water uptake.

Fractions of winter precipitation found in bulk and mobile soil waters at our site were only a few percent larger when calculated from throughfall than when calculated from open-field precipitation (Figure 6). Such several-percent differences would probably not substantially affect any conclusions that would be drawn concerning the seasonal origins of soil waters. However, the isotopic differences between precipitation, throughfall, and stemflow can be much larger over shorter time scales, leading to greater uncertainty in inferences, such as hydrograph separations, that are drawn from shorter-term isotopic variations.

In summary, our study documents isotopic offsets between precipitation, throughfall and stemflow. These offsets vary seasonally and between individual precipitation events, and they may have implications for tracer-aided assessments of seasonality and water ages in soils, streamflow and plant water.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

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

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REFERENCES

Allen, S. T., Aubrey, D. P., Bader, M. Y., Coenders-Gerrits, M., Friesen, J., Gutmann, E. D., Guillemette, F., Jiménez-Rodríguez, C., Keim, R. F., Klamerus-Iwan, A., Glenda, M.-L., Philipp, P., Qualls Robert, G., Bart, S., Aron, S., & Van Stan, J. T., II. (2020). Key questions on the evaporation and transport of intercepted precipitation. In *Precipitation partitioning by vegetation* (pp. 269–280). Springer. https://doi.org/10.1007/978-3-030-29702-2_16

Allen, S. T., Keim, R. F., Barnard, H. R., McDonnell, J. J., & Renée, B. J. (2017). The role of stable isotopes in understanding rainfall interception processes: A review. *WIREs Water*, *4*(1), 1–17. https://doi.org/10.1002/wat2.1187

Allen, S. T., Keim, R. F., & McDonnell, J. J. (2015). Spatial patterns of throughfall isotopic composition at the event and seasonal timescales. *Journal of Hydrology*, *522*, 58–66. https://doi.org/10.1016/j.jhydrol.2014.12.029

Allen, S. T., Kirchner, J. W., Braun, S., Siegwolf, R. T. W., & Goldsmith, G. R. (2019). Seasonal origins of soil water used by trees. *Hydrology and Earth System Sciences*, *23*(2), 1199–1210. https://doi.org/10.5194/hess-23-1199-2019

Allen, S. T., von Freyberg, J., Weiler, M., Goldsmith, G. R., & Kirchner, J. W. (2019). The seasonal origins of Streamwater in Switzerland. *Geophysical Research Letters*, *46*(17–18), 10425–10434. https://doi.org/10.1029/2019GL084552

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*, *22*(5), 2881–2890. https://doi.org/10.5194/hess-22-2881-2018

Bernhard, F., Floriancic, M. G., Treydte, K., Gessler, A., Kirchner, J., & Meusburger, K. (2023). Tree- and stand-scale variability of xylem water stable isotope signatures in mature beech, oak, and spruce. *Ecohydrology*. https://doi.org/10.22541/au.168310028.82017826/v1

Brinkmann, N., Eugster, W., Buchmann, N., & Kahmen, A. (2019). Species-specific differences in water uptake depth of mature temperate trees vary with water availability in the soil. *Plant Biology*, *21*(1), 71–81. https://doi.org/10.1111/plb.12907

Brodersen, C., Pohl, S., Lindenlaub, M., Leibundgut, C., & von Wilpert, K. (2000). Influence of vegetation structure on isotope content of throughfall and soil water. *Hydrological Processes*, *14*(8), 1439–1448. https://doi.org/10.1002/1099-1085(20000615)14:8<1439::AID-HYP985>3.0.CO;2-3

Carlyle-Moses, D. E., & Gash, J. H. C. (2011). Rainfall interception loss by Forest canopies. In *Forest hydrology and biogeochemistry* (pp. 407–423). Springer. https://doi.org/10.1007/978-94-007-1363-5_20

Cayuela, C., Llorens, P., Sánchez-Costa, E., & Latron, J. (2018). Modification of the isotopic composition of rainfall by throughfall and stemflow: The case of scots pine and downy oak forests under Mediterranean conditions: Isotopic modification of rainfall by canopy interception processes. *Ecohydrology*, *11*(8), e2025. https://doi.org/10.1002/eco.2025

Dawson, T. E., Mambelli, S., Plamboeck, A. H., Templer, P. H., & Tu, K. P. (2003). Stable isotopes in plant. *Ecology*, *33*, 507–559. https://doi.org/10.1146/annurev.ecolsys.33.020602.095451

Dewalle, D. R., & Swistock, B. R. (1994). Differences in oxygen-18 content of throughfall and rainfall in hardwood and coniferous forests. *Hydrological Processes*, *8*(1), 75–82. https://doi.org/10.1002/hyp.3360080106

Floriancic, M. G., Allen, S., & Kirchner, J. (2023). *Isotopic evidence for seasonal water sources in tree xylem and forest soils*. Authorea Preprints. https://doi.org/10.22541/au.169211345.57427570/v1

Floriancic, M. G., Allen, S. T., Meier, R., Truniger, L., Kirchner, J. W., & Molnar, P. (2022). Potential for significant precipitation cycling by forest-floor litter and deadwood. *Ecohydrology*, *16*(2), e2493. https://doi.org/10.22541/au.166209855.56534808/v1

Gat, J. R., & Tzur, Y. (1967). Modification of the isotopic composition of rainwater by processes which occur before groundwater recharge. https://www.osti.gov/etdeweb/biblio/20898880

Goldsmith, G. R., Allen, S. T., Braun, S., Engbersen, N., González-Quijano, C. R., Kirchner, J. W., & Siegwolf, R. T. W. (2018). Spatial variation in throughfall, soil, and plant water isotopes in a temperate forest. *Ecohydrology*, *12*(2), e2059. https://doi.org/10.1002/eco.2059

Goldsmith, G. R., Allen, S. T., Braun, S., Siegwolf, R. T. W., & Kirchner, J. W. (2022). Climatic influences on summer use of winter precipitation by trees. *Geophysical Research Letters*, *49*(10), e2022GL098323. https://doi.org/10.1029/2022GL098323

Grundmann, M. H., Molnar, P., & Floriancic, M. G. (2023). Quantification of enrichment processes in throughfall and stemflow in a mixed temperate forest. *Hydrological Processes*. In review.

Harper, W. V. (2016). Reduced major Axis regression. In N. Balakrishnan, T. Colton, B. Everitt, W. Piegorsch, F. Ruggeri, & J. L. Teugels (Eds.), *Wiley StatsRef: Statistics reference online* (pp. 1–6). Wiley. https://doi.org/10.1002/9781118445112.stat07912

Hsueh, Y.-H., Allen, S. T., & Keim, R. F. (2016). Fine-scale spatial variability of throughfall amount and isotopic composition under a hardwood forest canopy. *Hydrological Processes*, *30*(11), 1796–1803. https://doi.org/10.1002/hyp.10772

Ikawa, R., Yamamoto, T., Shimada, J., & Shimizu, T. (2011). Temporal variations of isotopic compositions in gross rainfall, throughfall, and stemflow under a Japanese cedar forest during a typhoon event. *Hydrological Research Letters*, *5*, 32–36. https://doi.org/10.3178/hrl.5.32

Jasechko, S., Birks, S. J., Gleeson, T., Wada, Y., Fawcett, P. J., Sharp, Z. D., McDonnell, J. J., & Welker, J. M. (2014). The pronounced seasonality of global groundwater recharge. *Water Resources Research*, *50*(11), 8845–8867. https://doi.org/10.1002/2014WR015809

Jasechko, S., Wassenaar, L. I., & Mayer, B. (2017). Isotopic evidence for widespread cold-season-biased groundwater recharge and young streamflow across central Canada. *Hydrological Processes*, *31*(12), 2196–2209. https://doi.org/10.1002/hyp.11175

Kendall, C., & Caldwell, E. A. (1998). Chapter 2 – fundamentals of isotope geochemistry. In *Isotope tracers in catchment hydrology* (pp. 51–86). Elsevier. https://doi.org/10.1016/B978-0-444-81546-0.50009-4

Klamerus-Iwan, A., Link, T. E., Keim, R. F., & Van Stan, J. T., II. (2020). Storage and routing of precipitation through canopies. In E. Gutmann &

J. Friesen (Eds.), *Precipitation partitioning by vegetation: A global synthesis* (pp. 17–34). Springer International Publishing. https://doi.org/10.1007/978-3-030-29702-2_2
Klaus, J., & McDonnell, J. J. (2013). Hydrograph separation using stable isotopes: Review and evaluation. *Journal of Hydrology*, *505*, 47–64. https://doi.org/10.1016/j.jhydrol.2013.09.006
Knighton, J., Souter-Kline, V., Volkmann, T., Troch, P. A., Kim, M., Harman, C. J., Morris, C., Buchanan, B., & Walter, M. T. (2019). Seasonal and topographic variations in ecohydrological separation within a small, temperate, snow-influenced catchment. *Water Resources Research*, *55*(8), 6417–6435. https://doi.org/10.1029/2019WR025174
Kubota, T., & Tsuboyama, Y. (2003). Intra- and inter-storm oxygen-18 and deuterium variations of rain, throughfall, and stemflow, and two-component hydrograph separation in a small forested catchment in Japan. *Journal of Forest Research*, *8*(3), 179–190. https://doi.org/10.1007/s10310-002-0024-9
Landwehr, J. M., & Coplen, T. B. (2004). Line-conditioned excess: A new method for characterizing stable hydrogen and oxygen isotope ratios in hydrologic systems. Available at: http://inis.iaea.org/Search/search.aspx?orig_q=RN:36008379
Levia, D. F., Carlyle-Moses, D., & Tanaka, T. (2011). *Forest hydrology and biogeochemistry: Synthesis of past research and future directions*. Springer. https://doi.org/10.1007/978-94-007-1363-5
Liu, W. J., Liu, W. Y., Li, J. T., Wu, Z. W., & Li, H. M. (2008). Isotope variations of throughfall, stemflow and soil water in a tropical rain forest and a rubber plantation in Xishuangbanna, SW China. *Hydrology Research*, *39*(5–6), 437–449. https://doi.org/10.2166/nh.2008.110
Magh, R.-K., Eiferle, C., Burzlaff, T., Dannenmann, M., Rennenberg, H., & Dubbert, M. (2020). Competition for water rather than facilitation in mixed beech-fir forests after drying-wetting cycle. *Journal of Hydrology*, *587*, 124944. https://doi.org/10.1016/j.jhydrol.2020.124944
Martinetti, S., Molnar, P., Carminati, A., & Floriancic, M. (2023). Plant hydraulic traits and water use strategies modulate root water uptake and transpiration in beech and spruce. *Authorea*. https://doi.org/10.22541/au.169999127.74763157/v1
Nehemy, M. F., Maillet, J., Perron, N., Pappas, C., Sonnentag, O., Baltzer, J. L., Laroque, C. P., & McDonnell, J. J. (2022). Snowmelt water use at transpiration onset: Phenology, isotope tracing, and tree water transit time. *Water Resources Research*, *58*(9), e2022WR032344. https://doi.org/10.1029/2022WR032344
Pinos, J., Flury, M., Latron, J., & Llorens, P. (2023). Routing stemflow water through the soil via preferential flow: A dual-labelling approach with artificial tracers. *Hydrology and Earth System Sciences*, *27*(15), 2865–2881. https://doi.org/10.5194/hess-27-2865-2023
Pinos, J., Latron, J., Nanko, K., Levia, D. F., & Llorens, P. (2020). Throughfall isotopic composition in relation to drop size at the intra-event scale in a Mediterranean scots pine stand. *Hydrology and Earth System Sciences*, *24*(9), 4675–4690. https://doi.org/10.5194/hess-24-4675-2020
Pinos, J., Llorens, P., & Latron, J. (2022). High-resolution temporal dynamics of intra-storm isotopic composition of stemflow and throughfall in a Mediterranean scots pine forest. *Hydrological Processes*, *36*(8), e14641. https://doi.org/10.1002/hyp.14641
Rothfuss, Y., & Javaux, M. (2017). Reviews and syntheses: Isotopic approaches to quantify root water uptake: a review and comparison of methods. *Biogeosciences*, *14*(8), 2199–2224. https://doi.org/10.5194/bg-14-2199-2017
Snelgrove, J. R., Buttle, J. M., & Tetzlaff, D. (2020). Importance of rainfall partitioning in a northern mixed forest canopy for soil water isotopic signatures in ecohydrological studies. *Hydrological Processes*, *34*(2), 284–302. https://doi.org/10.1002/hyp.13584
Sprenger, M., Leistert, H., Gimbel, K., & Weiler, M. (2016). Illuminating hydrological processes at the soil-vegetation-atmosphere interface with water stable isotopes. *Reviews of Geophysics*, *54*(3), 674–704. https://doi.org/10.1002/2015RG000515
Sprenger, M., Stumpp, C., Weiler, M., Aeschbach, W., Allen, S. T., Benettin, P., Dubbert, M., Hartmann, A., Hrachowitz, M., Kirchner, J. W., McDonnell, J. J., Orlowski, N., Penna, D., Pfahl, S., Rinderer, M., Rodriguez, N., Schmidt, M., & Werner, C. (2019). The demographics of water: A review of water ages in the critical zone. *Reviews of Geophysics*, *57*(3), 800–834. https://doi.org/10.1029/2018RG000633
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. https://doi.org/10.5194/hess-21-3839-2017
Stockinger, M. P., Lücke, A., McDonnell, J. J., Diekkrüger, B., Vereecken, H., & Bogena, H. R. (2015). Interception effects on stable isotope driven streamwater transit time estimates. *Geophysical Research Letters*, *42*(13), 5299–5308. https://doi.org/10.1002/2015GL064622
Sun, Q., Klaus, V. H., Wittwer, R., Liu, Y., van der Heijden, M. G. A., Gilgen, A. K., & Buchmann, N. (2022). Water uptake patterns of pea and barley responded to drought but not to cropping systems. *Biogeosciences*, *19*(6), 1853–1869. https://doi.org/10.5194/bg-19-1853-2022
von Freyberg, J., Allen, S. T., Seeger, S., Weiler, M., & Kirchner, J. W. (2018). Sensitivity of young water fractions to hydro-climatic forcing and landscape properties across 22 swiss catchments. *Hydrology and Earth System Sciences*, *22*(7), 3841–3861. https://doi.org/10.5194/hess-22-3841-2018
von Freyberg, J., Knapp, J. L. A., Rücker, A., Studer, B., & Kirchner, J. W. (2020). Technical note: Evaluation of a low-cost evaporation protection method for portable water samplers. *Hydrology and Earth System Sciences*, *24*(12), 5821–5834. https://doi.org/10.5194/hess-24-5821-2020
Waring, R. H., & Running, S. W. (2007). *Forest Ecosystems* (3rd ed.). Elsevier. https://www.elsevier.com/books/forest-ecosystems/waring/978-0-12-370605-8
Xu, X., Guan, H., & Deng, Z. (2014). Isotopic composition of throughfall in pine plantation and native eucalyptus forest in South Australia. *Journal of Hydrology*, *514*, 150–157. https://doi.org/10.1016/j.jhydrol.2014.03.068

SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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