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The role of pre-event canopy storage in throughfall and stemflow by using isotopic tracers

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ABSTRACT

Stable isotopes can be a valuable tool for tracing the redistribution, storage, and evaporation of water associated with canopy interception of rainfall. Isotopic differences between throughfall and rainfall have been attributed to three mechanisms: evaporative fractionation, isotopic exchange with ambient vapor, and temporal redistribution. We demonstrate the potential importance of a fourth mechanism: rainfall mixing with water retained within the canopy (in bark, epiphytes, etc.) from prior rain events. Amount and isotopic composition (^{18}O and ^{2}H) of rainfall and throughfall were measured over a 3-month period in a Douglas-fir forest in the Cascade Range of Oregon, USA. The range of spatial variability of throughfall isotopic composition exceeded the differences between event-mean isotopic compositions of rainfall and throughfall. Inter-event isotopic variation of precipitation was high and correlated with the isotopic deviation of throughfall from rainfall, likely related to a high canopy/bark storage capacity storage bridging events. Both spatial variability of throughfall isotopic composition and throughfall–precipitation isotopic differences appear to have been controlled by the temporally varying influence of residual precipitation from previous events. Therefore, isotopic heterogeneity could indicate local storage characteristics and the partitioning of flow-paths within the canopy. Copyright © 2013 John Wiley & Sons, Ltd.

KEY WORDS canopy storage; stable isotope tracers; rainfall interception; spatial heterogeneity; temporal stability

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INTRODUCTION

Forest canopies are capable of intercepting large quantities of precipitation, altering the spatial and temporal inputs of precipitation to forested landscapes (Levia *et al*., 2011). The repeated drying and refilling of the interception storage can result in a large fraction (10–50%) of the gross precipitation (P_g) annually being lost to evaporation (Carlyle-Moses and Gash, 2011). The remaining water that is not evaporated flows down stems as stemflow (SF), and drips or splashes off of branches and leaf surfaces (Herwitz, 1987) as throughfall (TF), resulting in a patchy distribution of water inputs to the forest floor (Bouten *et al*., 1992; Keim *et al*., 2005; Staelens *et al*., 2006). These processes have major consequences for the hydrology (Gerrits *et al*., 2010; Hopp and McDonnell, 2011; Levia *et al*., 2011) and the ecology of forested watersheds (Navar and Bryan, 1990; Raat *et al*., 2002).

Studying TF and SF dynamics is a measurement challenge (e.g., Holwerda *et al*., 2006). Most field studies, as reviewed by Levia *et al*. (2011), have employed hydrometric techniques, but these are insufficient to resolve many details of storage and evaporation from canopies (Klaasen *et al*., 1998). Naturally occurring stable isotopes in water (^{18}O and ^{2}H) have been highly instructive as tracers in other areas of hydrology (e.g., Kendall and McDonnell, 1998) but have not generally been used to understand canopy interception processes. Although stable isotopes are commonly used for estimating evaporation (Gibson *et al*., 1996; Kubota and Tsuboyama, 2004), previous studies have found that the isotopic composition of throughfall is affected by complex exchange and mixing processes in the canopy rather than simply evaporation (Saxena, 1986; Dewalle and Swistock, 1994; Brodersen *et al*., 2000; Ikawa *et al*., 2011).

The details of these isotopic processes occurring with TF remain unclear. This is a problem because TF variations indicated by isotopic variations ultimately cascade through the entire hydrologic system, affecting soil water, groundwater, and stream water isotopic signatures (Gibson *et al*., 2000; Kubota and Tsuboyama, 2003). Previous TF isotope

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studies have focused on three factors that could drive the differences in isotopic composition of TF and P_g: evaporation from the canopy during or between storms (Saxena, 1986; Dewalle and Swistock, 1994); the selective canopy storage effect, where water is differentially retained or transmitted by the canopy throughout storms (Dewalle and Swistock, 1994; Brodersen *et al*., 2000; Ikawa *et al*., 2011); and isotopic exchange with ambient vapor in the canopy air space (Saxena, 1986; Kendall, 1993; Ikawa *et al*., 2011).

In humid climates such as the Pacific Northwest of the USA, substantial water may be retained in the canopy between events. This inter-event carryover is further facilitated by forests containing thick bark and dense epiphytes creating a complex system of spatiotemporally varying storage capacities and water residence times (Herwitz, 1985; Pypker *et al*., 2011). Previous studies have suggested that the complex network of canopy flowpaths and localized storage features results in a chemically heterogeneous TF input to the soil (Levia and Frost, 2006; Zimmerman *et al*., 2007). However, the role this pre-event moisture plays in the throughfall generation, chemistry, and routing is not well understood. Although previous studies have explored throughfall isotopic fractionation and time-shifts, no studies have explored these processes in terms of isotopic mixing.

Here, we examine the effect of residual moisture from previous events on TF-P_g isotopic differences and TF isotopic heterogeneity for several storms at the H. J. Andrews Experimental Forest in Oregon, USA. We hypothesized that the mixing of rainfall with pre-event canopy water strongly influences the isotopic composition of TF. We report $\delta^{18}O$ and $\delta^{2}H$ for incremental P_g, bulk TF of numerous collectors, and SF for a sequence of 11 events during the fall 2010 transition from the dry to wet season. We analyzed samples for spatial and temporal patterns that would be expected if stored canopy moisture was affecting throughfall chemistry.

METHODS

Site description

This study was conducted in watershed 1 (WS1) of the H. J. Andrews Experimental Forest in the western Cascade Range of Oregon. The steeply-sloped, 960 m^2 basin was clear-cut harvested in the late 1960s and is now covered with a dense canopy dominated by Douglas-fir (*Pseudotsuga menziesii*). Annual precipitation exceeds 2000 mm, with 80% falling mainly as rain between October and April. The climate, vegetation, management history, and geology of the H. J. Andrews and of WS1 have been extensively described in a previous work (e.g., Jones and Grant, 1996; Moore *et al*., 2004). Throughfall plots were located at 500 m elevation on a 75-m long section of a north–south transect near the stream outlet of WS1. All P_g was collected in a clearing 100 m distance from the TF plots. Meteorological data, including relative humidity and rainfall intensity, were measured at the H. J. Andrews benchmark meteorological station, 'Primemet' (Henshaw *et al*., 1998) located 500 m from the study plots.

Sample collection

TF and P_g were collected using 13 and 2 (respectively) commercially fabricated rain gages (EZ-read, Headwind Consumer Products) with a 7100-mm^2 funnel and a plastic float to reduce evaporation. All TF gages were placed under Douglas-fir trees. Additionally, SF was collected off of two 0.40-m-diameter Douglas-fir trees using polyvinyl chloride tubing halved longitudinally and sealed to each tree with silicone caulk (e.g., Herwitz, 1986) and routed into 20-l plastic containers. In addition to bulk TF and P_g collection, SF collection and passively collected incremental samples (Kennedy *et al*., 1979; McDonnell *et al*., 1990) of P_g, collected on a roughly 9-mm increment with a 28,000-mm^2 funnel, began during the third rain event. The volume of each TF, P_g, and P_g increment collector was measured and a 20 ml subsample was taken from each for isotope analysis.

Rainfall was sampled by collecting precipitation from the onset of precipitation until canopy drip ceased. Logistical constraints forced some sampling periods to last several days and consist of multiple consecutive storm events. Intra-event rain-free periods never exceeded 2 days. Potential for evaporation from collectors was low over this period with a mean relative humidity of 99%. This resulted in a total of 11 collection events (Table 1).

Analyses

All isotope data are expressed in terms δ values in units of parts per thousand (‰) with δ calculated:

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{VSMOW}}} - 1\right)$$

where VSMOW is the Vienna Standard Mean Ocean Water (Coplen *et al*., 2002), and R is the ratio of $^{18}O/^{16}O$ or $^{2}H/^{1}H$. Water samples were analyzed for $\delta^{2}H$ and $\delta^{18}O$ by using an off-axis cavity ringdown laser spectometer (Los Gatos Research, Mountain View, CA, USA) by the Institute for Water and Watersheds Collaboratory (Corvallis, OR, USA). Accuracies were 0.18 ± 0.07‰ and -1.02 ± 0.92‰ (mean ± standard error) for $\delta^{18}O$ and $\delta^{2}H$ respectively, calculated from measurements of interspersed standards during the analysis. The precision between repeated measures was 0.07‰ and 0.28‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively. In this paper, TF or SF $\delta^{18}O$ and d-excess values are often reported as Δ values, with the respective P_g value subtracted (i.e., TF $\Delta\delta^{18}O$ = TF $\delta^{18}O$ – P_g $\delta^{18}O$).

Table I. Depth, intensity, and isotope values of TF and P_g. Data are reported as mean ± *SD*. Δ indicates the difference between throughfall and gross precipitation.

		Rain (P_g)				Throughfall (TF)			TF-P_g differences		
Event	Date (in 2010)	Depth (mm)	Intensity (mm/h)	$\delta^{18}O$ (‰)	d-excess (‰)	Depth (mm)	$\delta^{18}O$ (‰)	d-excess (‰)	Loss (%)	$\Delta\delta^{18}O$ (‰)	Δd-excess (‰)
1	10-9 to 10-10	40	1.7	−6.7	11.7	30 ± 6	−6.7 ± 0.3	11.0 ± 0.4	23.8	0.0	−0.7
2	10-22 to 10-23	14	0.8	−9.7	10.3	10 ± 3	−8.5 ± 0.4	11.1 ± 0.6	27.6	1.3	0.8
3	10-23 to 10-24	62	2.9	−14.2	13.0	52 ± 9	−13.9 ± 0.4	11.2 ± 0.8	16.3	0.4	−1.8
4	10-24 to 10-27	82	1.7	−8.8	21.7	68 ± 22	−8.4 ± 0.4	20.5 ± 1.0	17.5	0.4	−1.2
5	10-27 to 11-2	43	0.8	−10.1	8.4	40 ± 27	−9.3 ± 0.9	10.0 ± 0.7	6.3	0.8	1.6
6	11-2 to 11-8	52	1.5	−15.4	9.6	43 ± 9	−15.0 ± 0.4	8.4 ± 2.2	17.4	0.4	−1.2
7	11-8 to 11-10	49	1.5	−10.9	16.7	46 ± 27	−10.5 ± 0.5	16.4 ± 2.5	5.0	0.5	−0.3
8	10-10 to 10-16	32	0.6	−6.2	11.8	30 ± 8	−6.2 ± 0.2	11.8 ± 1.1	4.6	0.1	0.0
9	11-16 to 11-19	45	2.0	−10.9	12.7	42 ± 21	−10.3 ± 0.3	12.8 ± 0.6	6.7	0.7	0.1
10	12-6 to 12-8	11	1.1	−9.9	15.0	9 ± 3	−11.0 ± 0.4	15.4 ± 1.2	20.9	−1.1	0.4
11	12-8 to 12-10	49	1.7	−7.5	18.7	44 ± 27	−7.2 ± 0.3	17.1 ± 1.5	9.3	0.3	−1.7

We calculated d-excess = $\delta^2H - 8(\delta^{18}O)$ for all samples. This index describes deviation from the meteoric water line (MWL) and can be used to indicate kinetic (i.e., non-equilibrium) fractionation effects of evaporation (Gat, 1996) (Figure 1). Increased kinetic fractionation at lower humidities decreases the slope of δ^2H versus $\delta^{18}O$ and thus increases deviations from the MWL (Gat, 1996). Because humidity was always high and equilibrium processes do not change d-excess (Dansgaard, 1964), we used d-excess as an indicator of mixing rather than an indicator of evaporation. Others have successfully used d-excess for the tracing of mixing processes (Machavaram *et al*., 2006) and distinguishing end-members and their residence times (Gibson *et al*., 2000; Fitzgerald *et al*., 2003); here we apply this concept at a smaller scale.

Statistical analyses were performed using MATLAB (MathWorks Natick, MA, USA), and Sigmaplot 12.0 (SYSTAT, Chicago, IL, USA). Mixing model calculations by using δ^2H signatures were performed with IsoSource (Phillips and Gregg, 2003; EPA Western Ecology Division, Corvallis, OR, USA) to quantify contributions of P_g increments to the bulk TF signatures.

Time-stability plots. The temporal stability of the spatial pattern of depth, $\delta^{18}O$, and d-excess of throughfall were analyzed by standardized time-stability plots (Keim *et al*., 2005). Data points were standardized for each event by subtracting the event mean and dividing by the event standard deviation. Because the data were not normally distributed, a Tukey honestly significant difference test was used among rank-transformed means for multiple comparisons if the non-parametric Kruskall–Wallis (KW) test indicated a general effect of sampling location. Each collector was tested to determine whether it was significantly different from each of the other collectors ($p < 0.05$).

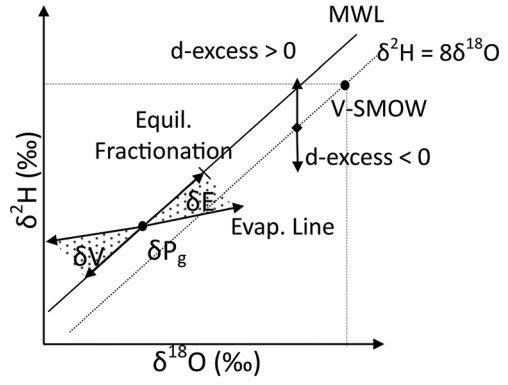

Figure 1. Conceptual diagram of water fractionation processes plotted in dual isotope space. δP_g is the precipitation, falling along the meteoric water line (MWL) with a d-excess of 10. δE is the isotopic composition of an evaporated source, and δV indicates the vapor coming from this source. Adapted from Gat (1996).

RESULTS

Overview

Over the entire measurement period, interception loss (IL = P_g − TF) was 14% of P_g (excluding stemflow). TF depth variability between collectors was fairly consistent among events. The mean TF depth was 86 ± 37% (mean ± *SD*) of P_g, the mean minimum collector depth was 39% of P_g, and the mean maximum collector depth was 179% of P_g (Figure 2).

The mean TF $\Delta\delta^{18}O$ was 0.3 ± 0.7‰ (mean ± *SD*). The mean range of spatial variation was 1.6‰ $\delta^{18}O$ over all events and as high as 3.7‰ in collection period five (P5) (Figure 2). The TF $\Delta\delta^{18}O$ tended to be positive for most events (Table 1) but was significantly negative for one event ($p = 0.003$).

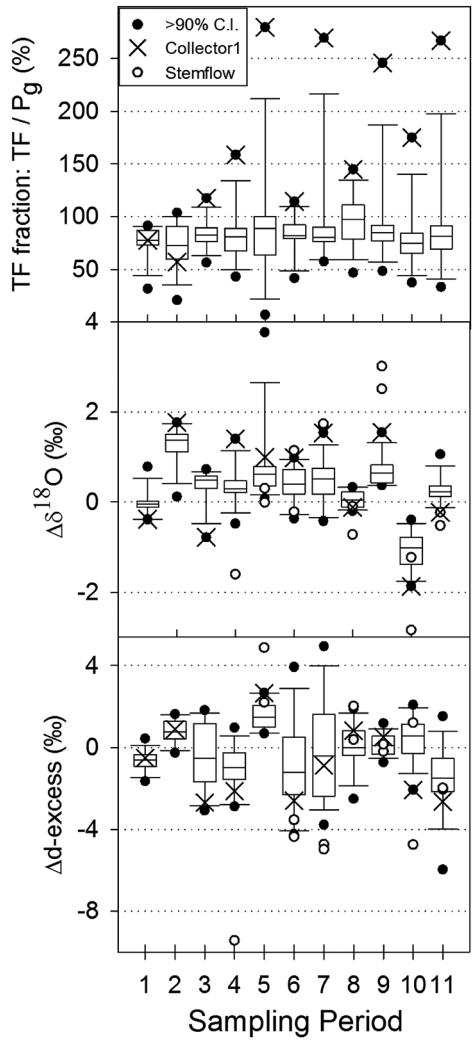

Figure 2. Box-plots for throughfall depth fraction (TF/P_g), relative Δ(TF-P_g or SF-P_g) $\delta^{18}O$, and d-excess for 11 events in the fall of 2010. The box-plots show the mean, upper and lower quartiles, 90% confidence interval, and filled circles indicate throughfall samples outside the 90% CI. The values for one consistent outlier throughfall collector are marked. Dates of sampling periods are listed in Table 1.

Values of d-excess for most rain and throughfall samples were above or near 10‰, roughly the d-excess of the global MWL (Kendall and Caldwell, 1998). The TF Δd-excess greatly varied spatially within certain events with simultaneous positive and negative values of TF Δd-excess. There was little consistency in deviation of d-excess from event-mean TF and P_g (mean ± SD = −0.4 ± 1.0‰). The mean spatial range in TF Δd-excess over all events was 5.0‰ and exceeded 8‰ in two collection periods (P6 and P7).

One TF collector (Collector1) that was located under a crown with dense epiphyte cover exhibited TF behavior unique from the other collectors (Figure 2). After the third event, Collector1 consistently received TF depths exceeding the 90% confidence interval around the mean depth, illustrating a threshold behavior associated with the fall wet-up period. In addition to frequently receiving very high TF depths, Collector1 also tended to have the largest deviation from the isotopic composition of P_g but not in a consistent direction.

The funneling ratio, calculated as SF volume/(P_g × basal area of stem) (Levia *et al.*, 2011), was 0.7 ± 0.5 (mean ± SD). SF $\Delta\delta^{18}O$ for was 0.09 ± 1.6‰. In most events where SF was measured (Figure 2), the absolute value of SF $\Delta\delta^{18}O$ was greater than the 90% CI of TF, but not consistently heavier or lighter than TF. The direction of deviation of SF Δd-excess also was inconsistent (mean ± SD = −2.2 ± 4.0‰).

The events with the lowest depths generally had the highest isotopic deviation from rainfall; however, there was no statistically significant relationship between the event size and the absolute value of TF $\Delta\delta^{18}O$ ($r^2 = 0.31$, $p = 0.07$). P10, the event with the least depth, was also the only event with significant net depletion ($\Delta\delta^{18}O$ = −1.1‰, $p = 0.003$); TF Δd-excess was not different from P_g for this event (Table 1). Event-mean interception loss was a poor predictor of TF $\Delta\delta^{18}O$ ($r^2 = 0.01$, $p = 0.78$) and d-excess ($r^2 = 0.06$, $p = 0.48$). TF $\Delta\delta^{18}O$ was also not correlated with the event size ($r^2 = 0.05$, p = 0.52), or the precipitation intensity ($r^2 < 0.01$, $p = 1$). TF Δd-excess was inversely correlated with both event depths ($r^2 = 0.38$, $p < 0.05$) and precipitation intensity ($r^2 = 0.67$, $p < 0.05$), which is the opposite of what would be expected if evaporation was causing the differences in TF Δd-excess.

Precipitation often was the most depleted in ^{18}O and ^{2}H in the middle of storm periods, and frequently the last incremental sample was more enriched than the mean P_g bulk sample (the 'V' pattern described by Kendall (1993)) (Table 2). Of the events when incremental samples were collected, only two out of the seven events did not display the V pattern (P7, P9).

The spatial distribution of the TF depth was generally persistent from event to event (Figure 3A). That is, high-depth locations remained high-depth and low-depth locations remained low-depth. On average, depth at each collector was significantly different from 2.15 other collectors (KW test, $\chi^2 = 67.68$, $df = 12$, $p < 0.001$). In contrast, patterns between collectors were not stable for either $\delta^{18}O$ or d-excess: the averaging of nonpersistent normalized values caused the means to be almost constant across collectors (Figure 3B and C). A regression of mean normalized positive deviations versus mean normalized negative deviations of ^{18}O for each collector yielded an r^2 of 0.71, demonstrating that collectors with a high $\delta^{18}O$ deviation for one event tended to have large deviations in both directions around the mean for other events. No collectors were significantly different from each other in either TF $\delta^{18}O$ or d-excess (KW test, $\chi^2 = 5.82$, $p = 0.925$; KW test, $\chi^2 = 13.49$, $p = 0.3343$, respectively).

We also assessed the ^{18}O time stability (Figure 3D) for only events where the last increment was more enriched

Table II. Sequential δ^2H and $\delta^{18}O$ values of rainfall sampled by an approximately 9-mm volume increment for seven rain events. Data are reported in units of parts per thousand.

	Events													
Increment	4		5		6		7		8		9		11	
	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H
1	−7.1	−37	−7.5	−52	−9.7	−73	−8.5	−49	−6.3	−37	−6.8	−41	−6.5	−34
2	−8.7	−45	−11.8	−88	−15.8	−122	−10.4	−69	−7.4	−49	−9.1	−59	−7.3	−41
3	−8.1	−41	−12.9	−93	−20.6	−160	−10.4	−68	−5.1	−31	−12.8	−92	−7.9	−50
4	−6.1	−27	−12.3	−87	−23.5	−181	−11.3	−75	−4.2	−20	−14.5	−104	−6.5	−38
5	−8.2	−47	−5.8	−35	−9.8	−63	−12.2	−87			−13.1	−88	−7.4	−40
6	−9.8	−59			−8.8	−49	−12.0	−85					−7.2	−37
7	−11.9	−77												
8	−10.0	−59												
9	−8.2	−46												

than the average P_g (V storms). However, we again observed that normalized $\delta^{18}O$ values were not persistent, conflicting with the selective storage process described by Dewalle and Swistock (1994).

Residual canopy storage effect on throughfall

Isotopic compositions of TF and P_g indicated previous events have an effect on subsequent rain events. The Δd-excess of both TF and SF was negatively correlated with the difference between the d-excess of P_g and the P_g for the previous event ($r^2 = 0.58$ and $r^2 = 0.79$, respectively) (Figure 4). There was a weaker, but also negative, correlation for TF $\Delta\delta^{18}O$ assessed the same way. For events following a more enriched event, TF $\Delta\delta^{18}O$ (TF $\Delta\delta^{18}O = 0.56 \pm 0.08‰$) was greater ($p = 0.02$) than $\Delta\delta^{18}O$ of TF for events following more depleted events (TF$\Delta\delta^{18}O = 0.33 \pm 0.05‰$) (mean ± *SE*). The relationship between SF and TF $\Delta\delta^{18}O$ and Δd-excess, and the differences between events suggest the potential importance of carryover between events.

Regarding isotopic spatial variability, it was difficult to explain the observed deviations of SF and Collector1 from the other collectors without consideration of an additional moisture source. We considered each plot in Figure 5 as a mixing diagram, where both TF and SF measurements must have been a mixture of the contributing end-members, which included incremental P_g and the final increment of P_g of the previous event (to account for residual stored moisture). Isotopic composition of TF at most collectors was bracketed by many incremental rainfall samples, so the relative proportions could not be calculated. However, TF Collector1 and SF were frequently outside the cluster of other TF point-measurements. Using Isosource (Phillips and Gregg, 2003) for analyzing contributions from sources, not including the previous event's last increment, TF for event P7 at Collector1 had to have received between 45% and 73% of its volume from the first of the six total increments sampled. Similarly, P11's third P_g increment would need to contribute 68–83% of stemflow to explain the SF's isotopic composition, and for P4, 67–88% of stemflow appears to have come from the seventh of nine increments to explain the SF isotopic composition.

Including the residual moisture (i.e., the previous event's last increment or mean when increments were not available) as an end-member reduced the previously heavily-weighted increments to a potential minimum contribution of zero percent; that is, no longer did an unreasonable fraction of bulk SF or TF appear to come from single increments. The contributions of those single increments were reduced dramatically in these examples because SF, and often Collector1, deviated from P_g in the same direction as the isotopic composition of the previous event (Figure 5). The only event where SF did not deviate from P_g was P6, which followed a 4-day drying period, minimizing the residual storage. The effect of this drying period was also illustrated by the relatively lower depth of TF at Collector1, likely because the storage deficit had to be refilled.

DISCUSSION

Residual moisture as a control over throughfall isotopic composition

Our observations suggest that residual canopy moisture is important to the resulting isotopic composition of TF and SF. The frequent rain, high humidity, and dense coniferous canopy of the Pacific Northwest may maximize the residual storage effect on isotopic composition of throughfall, especially because of epiphytes (Pypker *et al.*, 2006) and high specific storage in the foliage (Keim *et al.*, 2006). These conditions are likely to increase the legacy of

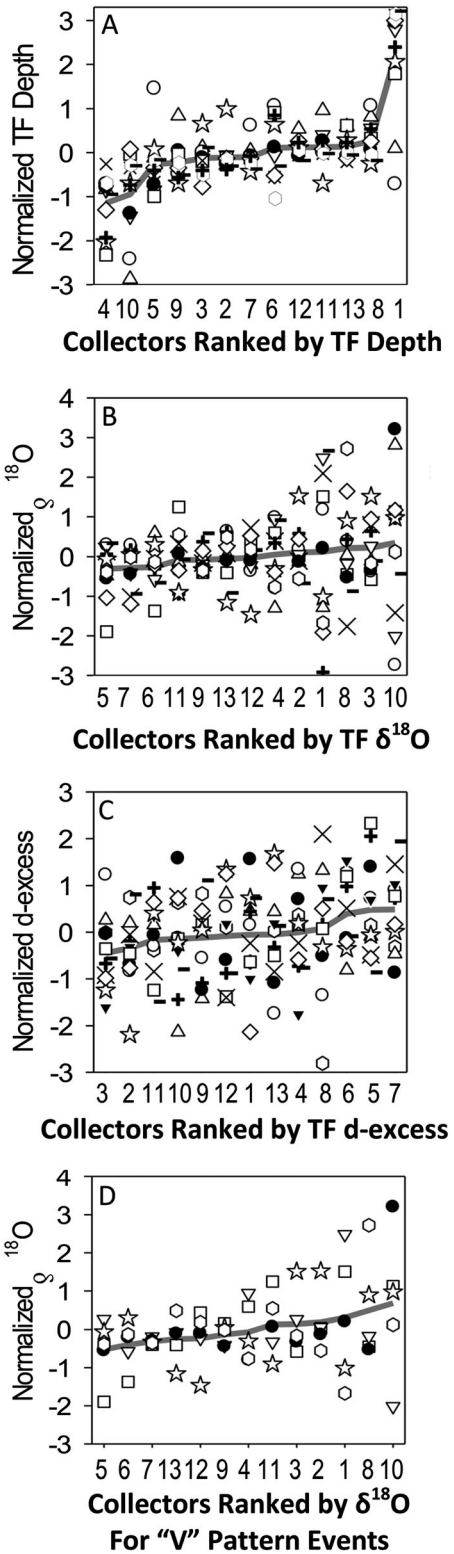

Figure 3. (A–C) Time-stability plots for all measured events. Each point refers to a single standardized measurement at a single location, and symbols refer to sampling events: Δ, P1; ○, P2; +, P3; ▽, P4; ●, P5; □, P6; ×, P7; ☆, P8; -, P9; ◇, P10; ⬡, P11. Collectors are ranked by the mean value of the dependent variable for each collector, shown by the gray line. (D) Time-stability plot for 'V' storms. V storms are storms ending with the last increment of rain being more enriched than the bulk rainfall.

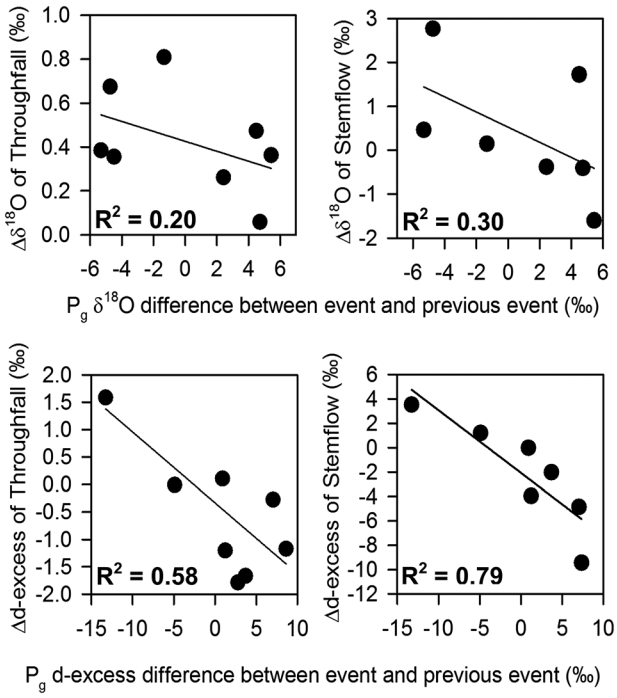

Figure 4. Previous event differences versus TF-P_g differences. $\Delta\delta^{18}O$ (top) and Δd-excess (bottom) of throughfall (left) and stemflow (right) are plotted against, respectively, the difference of the previous event's $\delta^{18}O$ (top) and d-excess (bottom) subtracted from each event. P1 and P10 were excluded because we did not have data for the immediately preceding event. P2 was excluded because it occurred 12 days after P1.

moisture from the previous events demonstrated by our results showing that the event-mean Δd-excess of TF and SF were linearly related to the d-excess difference between each event and its preceding event (Figure 4). After the second rain event, the duration of rainless periods were generally less than 1 day, and relative humidity was always high. Even though we expect that most leaf surfaces dried between events, bark and epiphytes can hold substantial water and have morphologies that decrease evaporation (Pypker *et al.*, 2006; Pypker *et al.*, 2011).

Although this residual canopy storage might be expected to fractionate between events, effects of isotopic differences among storms (mean 4.1‰ $\delta^{18}O$ and 5.5‰ d-excess) were larger than the plausible magnitude of effects of fractionation by evaporation or isotopic exchange (Gat and Tzur, 1967). Isotopic exchange would have little effect if the vapor in the canopy air space is nearly in equilibrium with the residual moisture (Dansgaard, 1964). This enabled d-excess to be used as a robust index for analyzing mixing, because fractionation effects on d-excess are minimal during high humidity conditions. The weaker relationships for $\Delta\delta^{18}O$ that we observed (Figure 4) were likely due to confounding fractionation effects.

The role of bark and epiphytes may cause spatial variability in both the canopy storage capacity and the

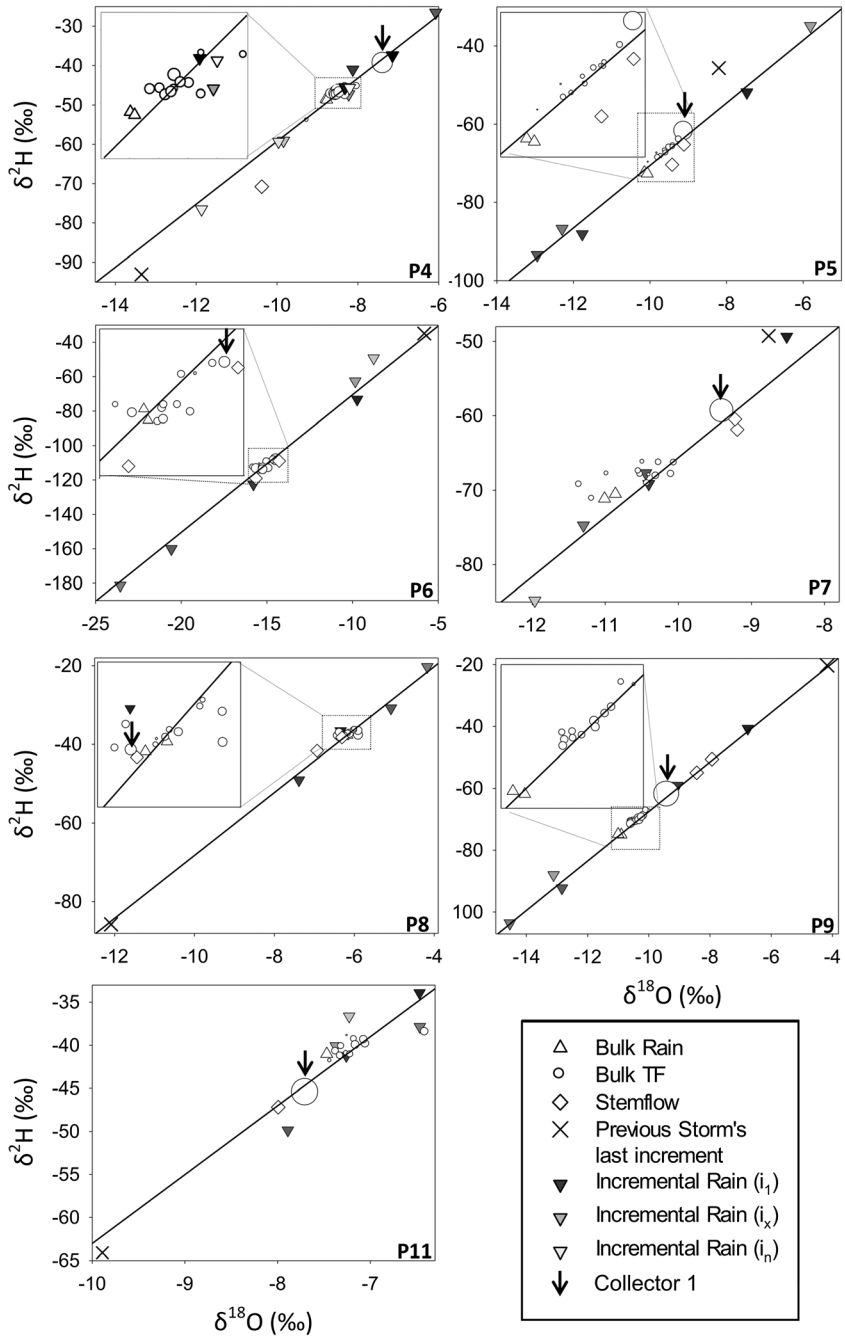

Figure 5. Dual isotope plots for rain, throughfall, and stemflow in select events. Event MWLs for precipitation are indicated by lines with a slope of 8 and intersecting the origin at the mean d-excess for that event. Diameter of bulk TF symbols are scaled to relative depth (within-event). Incremental samples of rainfall are shaded lighter with successive increment.

degree of mixing with residual moisture; this could explain the observed isotopic heterogeneity of TF (Figure 2) and persistent locations of large isotopic deviations (Figure 3). Following our conceptual model of residual moisture carryover, the direction of deviation should be controlled by the relative difference between each event and the previous event. Thus we would not expect a persistent spatial pattern of higher and lower isotopic compositions, but instead, collectors under areas of higher canopy storage would be more affected by residual moisture and, therefore, a greater deviation in either direction.

Measurements from Collector1 and stemflow, the consistent isotopic outliers, were particularly demonstrative of the effect of residual moisture on isotopic spatial variability. Mixing-model analysis indicated the large isotopic deviation

of SF and Collector1 from the other TF measurements were only reasonable when accounting for the effects of the previous event as an additional end-member. Otherwise, disregarding fractionation, both TF and SF would have appeared to have been primarily sourced from small increments of the whole precipitation events. SF and Collector 1 also increased yield as the tree surfaces wet up through the season, indicative of a large storage deficit to overcome, which, once saturated, would be a larger pool for mixing with and explains why the biggest isotopic deviations were often observed in SF and the Collector 1.

The importance of long-duration storage and within-canopy flowpaths adds a level of complexity to the TF/SF generation process that has been rarely investigated. As one key example of its importance, Levia and Herwitz (2005) found that rough-barked *Quercus rubra* had higher bark storage than two other hardwood species yet also produced more SF volume and solute loads. They attributed this finding to bark morphology and the residence time of water in the bark, which coheres with our observations of the importance of long-term storage controlling TF/SF characteristics.

Implications of residual storage

The observed isotopic heterogeneity of TF indicated the complexity of canopy storage, consisting of areas of high storage capacity that were temporally varying in deficit from event to event. Saturation of canopy flowpaths can result in the conversion of stemflow to throughfall, which can be even further increased by rough surface features enabling dripping (Levia *et al*., 2011). The pre-event moisture evident in this system could maintain nearly saturated conditions, explaining the persistence of the Collector1 depth and isotopic differences. Pre-event moisture may also explain the low funneling ratios observed in perhumid Douglas-fir forests (Rothacher, 1963).

Canopy water with extended residence time and mixing in epiphytes and branch surfaces may have ecological and biogeochemical significance (Puckett, 1991; Levia and Herwitz, 2005; Zimmerman *et al*., 2007). Trees' roots may cluster to optimize usage of zones in soil with more moisture or nutrients; thus, exploitation of the rhizoshpere may be controlled by TF and SF (Kazda and Schmid, 2009). We hypothesize TF stable isotope signatures may indicate persistent biogeochemically distinct hot spots.

Aside from Collector1 and the SF collectors, Figure 5 indicates that the other of the collectors mostly received TF that had less interaction with residual storage. Rather than being composed of rainfall mixed with pre-event storage, isotopic composition in these collectors may have been dominated by interaction with intra-canopy vapor instead, as Kendall (1993) also hypothesized. Droplets that originate from drip points at loci of storage in the canopy are much larger than those originating from splash interactions (Moss and Green, 1987; Dunin *et al*., 1988; Murakami, 2006) and generally larger than raindrops for this region (Mueller and Sims, 1968), so that equilibration of isotopic composition with canopy vapor is much less rapid (Friedman *et al*., 1962).

Effects of selective storage and evaporative fractionation

If residual storage alone exerted control over TF-P_g differences, these differences would average out to zero over an extended period of measurement, which was not what we observed. Therefore, other interception and isotope processes affect the isotopic composition of TF, but exactly which processes remain unclear. In particular, our results do not demonstrate the effects of evaporative fractionation or selective storage, although it is well known that both evaporation (Carlyle-Moses and Gash, 2011) and time-shifts (Herwitz, 1987; Keim and Skaugset, 2004), which could result in selective storage, do take place as part of the interception process.

Evaporation. Previous studies have concluded that evaporation was not a primary control over TF-P_g isotopic differences (DeWalle and Swistock, 1994; Brodersen *et al*., 2000) that corroborates with our results: event-mean interception loss was a poor predictor of TF $\Delta\delta^{18}O$ and Δd-excess. Additionally, if the time stability plots showed the direction of isotopic deviation was temporally stable, this might have indicated evaporative fractionation controlling the distribution because we would expect relative evaporation rates to be a function of intra-canopy location. However, they were not stable (Figure 3).

The mismatch between hydrometric evidence of evaporation and lack of isotopic fractionation (i.e., enrichment and deviation from the MWL) suggests that equilibrium exchange between storage and vapor at high humidity controlled isotopic composition of TF (Kendall, 1993). If vapor exchange overwhelms the evaporative influence (Saxena, 1986), it may be more important to determine how variability in exchange could affect TF isotopic composition, which also remained undetermined. However, little is known about within-canopy variations of the evaporation rate, although it undoubtedly varies due to differences in air movement (Daudet *et al*., 1999) and radiation in the canopy.

Selective storage. Selective storage has been identified by Dewalle and Swistock (1994) and Brodersen *et al*. (2000) as the reason why TF's isotopic composition is occasionally more enriched in heavy isotopologues than P_g. Dewalle and Swistock (1994) noted that the end of a rainstorm is usually the most isotopically depleted (Pionke and Dewalle, 1992), and precipitation at the end of storm remains intercepted and does not contribute to TF. More of our measured sampling

periods followed a V pattern, with which this previously described selective storage process would have resulted in TF being isotopically lighter than P_g. However, TF $\delta^{18}O$ was the same as P_g or heavier for all of the five V pattern events (P4, P5, P6, P8, and P11), suggesting that selective storage did not cause the TF-P_g isotopic differences. Additionally, the mixing model analysis indicated residual storage as an appropriate end-member, because no reasonable mixture of increments matched throughfall so time-varying bypass of the canopy cannot explain observed TF and SF isotopic compositions (Figure 5).

The lack of time stability of paired depth and $\delta^{18}O$ in TF is also useful evidence of whether selective storage was a major control on the spatial variability. If the selective storage effect functions as described by Dewalle and Swistock (1994), then the spatial pattern of the throughfall amount should be persistent and cohere with the pattern of the throughfall depth. In storms with P_g following a persistent isotope temporal pattern (e.g., Rayleigh distillation or the V pattern), collectors below canopy with greater local storage capacity would consistently deviate more from P_g, because more of the end of the storm would remain intercepted. However, in the five storms with a V pattern of TF isotopic composition, Figure 3 D shows little temporal persistence of pattern in $\delta^{18}O$ and therefore conflicts with the hypothesis of Dewalle and Swistock (1994) describing selective storage as a systematic exclusion of the last rainfall increment.

Nevertheless, our observations do not negate the possibility of selective storage having an effect on isotopic composition of TF because there remains a considerable amount of heterogeneity not accounted for by the residual moisture effect, so it is clear that other processes are causing isotopic variations in TF. Brodersen *et al*. (2000) attributed strong isotopic heterogeneity to selective storage to explain why they observed light TF (as low as $-1.9‰$ $\Delta\delta^{18}O$) in one location of the catchment and heavier ($>1‰$ $\Delta\delta^{18}O$) in another location during the same event. Differences of this magnitude are not easily explained.

CONCLUSIONS

The goal of this study was to use isotopic tracers to understand the role of pre-event canopy water storage, selective storage, and evaporative fractionation. Our study, like others, shows that the isotopic composition of throughfall can be significantly different than that of rainfall and that there are rarely simple explanations for differences. We found that the spatial variability in isotopic composition of throughfall is very high (Table 1; Figure 2) and often exceeds the difference between bulk the rainfall and the mean throughfall. Our novel finding in this study was the apparent mixing between rainfall and residual storage and its effect on the isotopic composition of throughfall and stemflow. Thus, the spatial heterogeneity often found in throughfall isotopic composition, in this and likely other studies, appears in part to be a function of mixing with the residual storage–a mechanism previously unexplored in the throughfall isotope literature. Although the disentangling of the temporal elements of selective storage with spatial throughfall patterns illustrated by this study are by no means complete in the present work, our findings suggest that exploration of pre-event canopy storage effects may be an important avenue of new research as related to forest watershed ecohydrological and biogeochemical processes.

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