Advanced Review

The role of stable isotopes in understanding rainfall interception processes: a review

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The isotopic composition of water transmitted by the canopy as throughfall or stemflow reflects a suite of processes modifying rainfall. Factors that affect isotopic composition of canopy water include fractionation, exchange between liquid and vapor, and selective transmittance of temporally varying rainfall along varying canopy flowpaths. Despite frequent attribution of canopy effects on isotopic composition of throughfall to evaporative fractionation, data suggest exchange and selection are more likely the dominant factors. Temporal variability in canopy effects is generally consistent with either exchange or selection, but spatial variability is generally more consistent with selection. However, most investigations to date have not collected data sufficient to unambiguously identify controlling processes. Using isotopic data for improved understanding of physical processes and water routing in the canopy requires recognizing how these factors and processes lead to patterns of isotopic variability, and then applying this understanding toward focused data collection and analysis.

How to cite this article:
WIREs Water 2017, 4:e1187. doi: 10.1002/wat2.1187

INTRODUCTION

The details of water redistribution by the canopy are poorly understood, but have important implications for heterogeneities in water distribution and solute concentrations at the soil surface[1–3] and in the subsurface.[4–6] The path from canopy to the soil surface can affect infiltration patterns and the availability of water and solutes to plants.[5–9] Some of the resulting input heterogeneities to the soil are persistent in time,[2] but these patterns vary in scale from canopy elements (e.g., branch vs leaf)[10] to plots[1] to landscapes.[11] Little work has been done to describe the processes that control and link these patterns across scales, partially because conventional methods require empirical parameters to compensate for poor representations of the underlying physics controlling canopy water fluxes.[12]

We know that evaporation from forest canopies (interception loss) is important, accounting for 13–22% of precipitation[13] with interception losses typically being higher for small events. Forests with frequent small precipitation events and dense forest canopies have the highest annual interception losses (~50%).[14] While another important effect of interception is that vegetation redistributes precipitation and results in soil moisture spatiotemporal variability,[15] high variability impedes precisely estimating throughfall (TF) amount. For hydrological models, such spatial heterogeneity has often been

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Conflict of interest: The authors have declared no conflicts of interest for this article.

considered a source of uncertainty in quantifying evaporation (e.g., empirical linear models[16] and models based on bucket-storage concepts[17]).

Given the importance of these canopy effects on plot-scale hydrological, biogeochemical, and ecological processes, they need to be understood and considered in watershed scale models. However, the lack of mechanistic understanding of canopy water routing to the soil hinders its parameterization. Therefore, an important challenge in developing a next generation of canopy interception sub-routines for watershed models is to first refine our understanding of the physics that control processes currently missing from canopy bucket-storage models.

How can we better understand the physics of interception when direct measurement of key variables is prohibitively challenging with today's sensor technology? One approach is to study water movement processes through the canopy using isotope tracing. Tracers are important in hydrology to study processes and pathways,[18] but there has been little application to date in canopy interception research. In particular, the stable isotope composition of water (δ_w) may aid in progressing toward a mechanistic understanding of interception processes, as has occurred in other areas of hydrology at both relatively fine scales[19] and regional scales.[20]

While the body of literature using stable isotope tracers in canopy interception is small, it has nearly doubled in the past 5 years (Table 1). The primary focus of most work to date has been to better constrain δ_w inputs for soil and watershed modeling. However, there is still much to learn using δ_w to investigate the interception process itself. Here we review and synthesize previous stable isotope investigations in canopy interception. We focus on the multi-scale spatiotemporal variability of δ_w in TF, open precipitation (OP), and stemflow (SF). Our objective is to synthesize the intellectual progress made, the ambiguities that remain, and to identify ways to use stable isotopes to improve the physical understanding of canopy interception. We focus on the interception of rainfall and do not include cloud interception or frozen water interception in our review. We recognize that snow and cloud interception is important[46] yet under-studied,[1] and we direct readers to '*Further Readings*' section.

BACKGROUND: ISOTOPE PROCESSES IN PRECIPITATION

The isotopic processes of rainfall generation, here summarized from Clark and Fritz,[47] parallel those in effect during canopy interception. Precipitation δ_w is a function of the original water vapor source and fractionating processes associated with droplet generation and subsequent exchanges while falling through air masses (Figure 1(a)).[47] Fractionation (changes in relative abundance of heavy and light isotopes) occurs with phase changes and transport because lighter water molecules diffuse more rapidly and preferentially evaporate, while heavy water molecules preferentially condense. In saturated conditions [100% relative humidity (RH)], like during rain droplet formation, fractionation occurs under equilibrium at a temperature-dependent constant with the flux of liquid to vapor (evaporation) equaling the flux from vapor to liquid (condensation). The ratio of equilibrium fractionation factors for H and O is ~8 and defines the meteoric water line (MWL) of $\delta^2H = 8 \times \delta^{18}O + d$, where δ describes the difference in isotope abundance ratio ($^{18}O/^{16}O$ or $^2H/^1H$) relative to a standard (e.g., V-SMOW; Figure 1(a)); the intercept, known as the deuterium excess (d), is roughly 10‰ for the global meteoric water line (GMWL). Most atmospheric vapor is sourced from oceans, for which $d = 0$, but net evaporation (evaporation > condensation) includes diffusion into dryer air, a non-equilibrium (i.e., kinetic) fractionation process. Differential effects of kinetic fractionation on H versus O are small (compared to equilibrium fractionation) resulting in vapor from the ocean that is less enriched in δ^2H relative to $\delta^{18}O$ (compared to expectations for equilibrium conditions), explaining $d \approx 10‰$ for the GMWL.[47] Because evaporation includes molecular diffusion (kinetic fractionation), and it involves forward and back exchanges between liquid and vapor (equilibrium fractionation), high humidity results in more vapor–liquid exchange, maintaining fractionation rates close to equilibrium. Low humidity results in more prominent kinetic diffusion effects, with residual evaporated water falling on a lower slope evaporation line in dual isotope space (Figure 1(a) and (b)). Thus, d can indicate deviation from an established MWL and how evaporated water may be.[18] The δ_w of various water reservoirs depends on fractionation and their size. For example, evaporation from the ocean does not substantially affect the ocean δ_w because of its large size. However, ongoing condensation of water vapor from air masses and continual loss of the condensate result in precipitation that is increasingly depleted of heavy isotopes in what is known as the rainout effect, a Rayleigh distillation process.[18] Falling droplets undergo mass exchanges and isotopic fractionation as they rapidly exchange with the ambient atmosphere,[48] potentially with net evaporation

TABLE 1 | Reviewed Study Details: Number of Collectors (# of Cols); Number of Plots or Treatments × Collectors with * Indicating Samples Pooled Prior to Isotopic Analysis; Measurement Interval; Number of Intervals in the Study (# of Ints); Whether Sub-Interval Incremental Throughfall (TF), Stemflow (SF), or Open Precipitation (OP) Were Collected; Event (Interval) Scale; Maxima (Max), Minima (Min), Mean, and Mean of Absolute Value (Abs) of Single-Event TF–OP Differences, Plot Differences, and TF–SF Differences; and Maximum Range and Mean Range among Collectors. Isotope Values Are for $\delta^{18}O$ (‰). Some Details Were Not Specified (NS)

Site and Study Details							Event TF–OP Difference				Plot Differences among Plots			Event TF–SF Differences				Collector Ranges	
Authorship	Year	Location	# of Cols	Interval	# of Ints	Incremental?	Max	Min	Mean	Abs	Max	Mean	Abs	Max	Min	Mean	Abs	Max	Mean
Leopoldo[21,1]	1981	NW Brazil	NS	Event	14		0.97	−0.39	0.14	0.34				1.32[1]	−0.89[1]	0.29[1]	0.57[1]		
Saxena[22]	1986	SE Sweden	4*	Event	24		1.2	−0.4	0.30										
Kendall[23,2]	1993	SE USA	2 × 3*	Event	16	TF and OP	2.55	−0.49	0.38	0.39	0.37	0.1	0.13	0.02	−0.43	−0.16	0.17	2.76	0.5/1.32
Dewalle and Swistock[24,3]	1994	NE USA	3 × 10*	Event	16		1.62	−0.47	0.25		0.85	0.15							
Rice et al.[25,4]	1996	NE USA	2 × 3*	Weekly	75		3.50	−4.50	0.51	0.77	2.83	0.19	0.32						
Pichon et al.[26,5]	1996	S France	1–4	Event	31		1.39	−0.43	0.19	0.23								1.18	0.47
Brodersen et al.[27,6]	2000	S Germany	2 × 2 × 2 × 3*	Weekly	18		0.85	−0.55	0.18		0.26	−0.02	0.13	2.35	−1.06	0.1	0.98	2.14	0.80
Gibson et al.[28,7]	2000	W Canada	NS	Event	15	TF and OP	2.14	−2.79	−0.13	0.92									
Kubota and Tsuboyama[29,8]	2003	E Japan	2*	Event	6	TF, SF, and OP	0.94	−0.67	−0.20	0.63				−0.03	−1.92	−0.94	0.94		
Fitzgerald et al.[30,9]	2003	W Canada	2*	NS	11				0.20										
McGuire[10]	2005	NW USA	3	Event	3		0.46	0.14	0.24	0.24								0.57	0.39
Liu et al.[31,11]	2008	SE China	2 × 6*	Monthly	23						0.71	0.04	0.24	0.61	−0.20	0.07	0.20		
Ikawa et al.[32,12]	2011	S Japan	2*	Event	1	TF, SF, and OP	−0.05							−0.53					
Barnard et al.[33,13]	2012	NW USA	3*	3–4 mm	110[13]	TF and OP			−0.43										
Kato et al.[34]	2013	E Japan	20	Event	2		1.3	1.2	1.25	1.25								1.6	1.45
Liu et al.[35,n]	2013	C China	3 × 3*	Event	13		2.16	−1.83	0.53	0.71								2.41	0.97
Allen et al.[36]	2014	NW USA	13	Event	11	OP	1.3	−1.1	0.30	0.6				1.90	−2.38	0.19	1.27	3.7	1.6
Xu et al.[37,15]	2014	S Australia	2 × 20*	~18 days	17	OP	0.75	−0.96	−0.07	0.25	0.89	0.04	0.25						
Qu et al.[38]	2014	E China	1	Event	3	TF and OP	0.0	−0.43	−0.17	0.17									
Liu et al.[39]	2015	C China	3 × 3*	Event	4		1.20	0.30	0.63	0.63									
Allen et al.[40,16]	2015	NW USA	2 × 18	~Weekly	7		1.8	0.1	0.7	0.7	0.34	0.05	0.09					1.6	1.2
Stockinger et al.[41,17]	2015	W Germany	6*	~Weekly	51		1.29	−0.98	0.27										

(continued overleaf)

TABLE 1 | Continued

Site and Study Details							Event TF–OP Difference				Plot Differences among Plots			Event TF–SF Differences				Collector Ranges	
Authorship	Year	Location	# of Cols	Interval	# of Ints	Incremental?	Max	Min	Mean	Abs	Max	Mean	Abs	Max	Min	Mean	Abs	Max	Mean
Green et al.[42,18]	2015	NE USA	6*	14 days	23		1.68	−0.56	0.24	0.39									
Hsueh et al.[43]	2016	SE USA	100	Event	5													11.8	6.82

[1] All data were digitized from Figure 11 in Gat and Matsui 1981.[44] Data under TF–SF column are actually SF–OP.
[2] For SF, # of Ints = 3 with 16 collectors. Among TF collectors, # of Ints = 5 with 30 collectors (digitized from Figure 4); events were with six collectors otherwise. TF–OP means are amount-weighted.
[3] Plot differences were digitized from Figure 2. TF–OP means are amount-weighted.
[4] Precipitation site was 3 km away, so TF–OP differences are less reliable; only the more proximal Bear Branch site was used. TF–OP means are amount-weighted.
[5] All data were digitized.
[6] For SF, # of Ints = 8 with four collectors. TF 'Collectors' were three pooled collectors under Periphery or Center. 'Plot' refers to beech versus spruce. All but TF–OP differences were digitized from Figure 4. TF–OP means are amount-weighted.
[7] All were digitized from Figure 3. TF–OP means are amount-weighted.
[8] The six events are a subset of the study where SF (four events with two collectors), OP, TF were collected on same measurement interval. TF–OP means are amount-weighted.
[9] Event-level data were collected but not reported.
[10] Personal communication of unpublished data, collected alongside WS10 gages described by McGuire et al. 2005.[45] Samples were collected in three troughs for three events (23, 22, and 12 mm events) under old and young growth Douglas-fir forest. TF–OP means are amount-weighted.
[11] TF–OP differences are not included because they were not measured on same time interval. TF plot and TF–SF differences means are amount-weighted.
[12] 'Max' is of one event, digitized from Figure 1.
[13] All intervals were volumetric increments without distinct events (roughly seven over 20 days). Lower catchment data only presented because closer to open precipitation collector.
[14] 'Collectors' refers to three pooled collectors under a single tree. All digitized from Figure 5. TF–OP means are amount-weighted.
[15] TF–OP means are amount-weighted.
[16] Statistics described are only for 'Experiment 2'.
[17] Event differences are shown in study but mean was communicated directly (Stockinger, personal communication).
[18] A subset of the TF data until November 2007 were used as recommended (Green, personal communication).

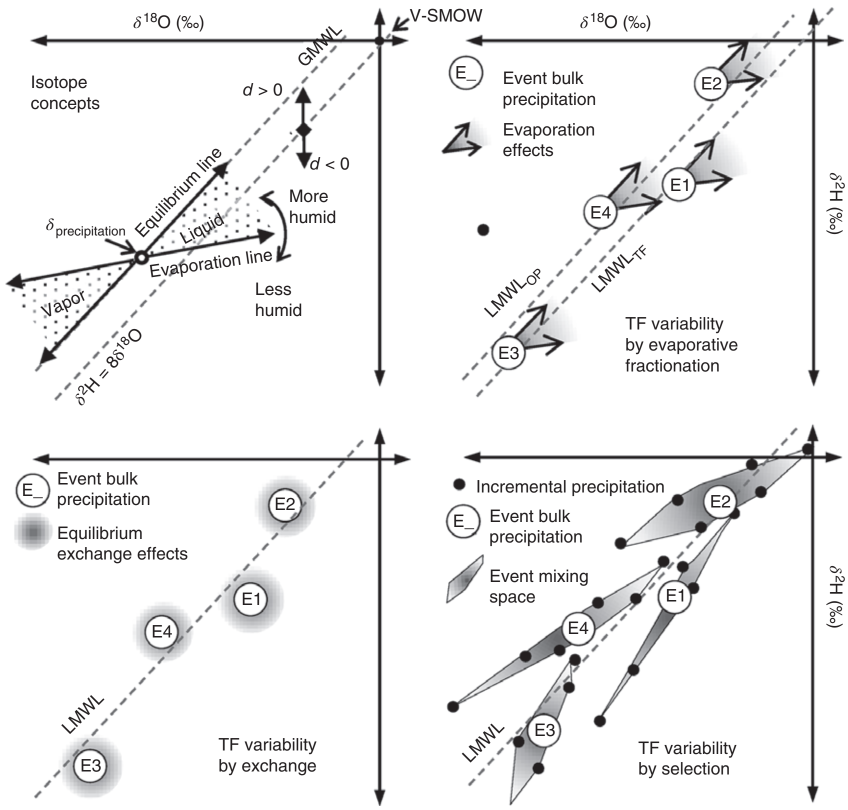

FIGURE 1 | Expected effects of canopy interception on δ^{18}O and δ^2H: (a) general isotope concepts including the global mean water line (GMWL), deuterium excess (d), and effects of kinetic and equilibrium fractionation on precipitation (δ_{precip}); (b) isotopic effects of evaporation on throughfall (TF) and the resulting theoretical local mean water lines of TF ($LMWL_{TF}$) and open precipitation ($LMWL_{OP}$); (c) isotopic effects of exchange on TF; and (d) isotopic effects of intra-event selection on TF.

effects (Figure 1(a)). Accordingly, δ_w varies unpredictably throughout and among precipitation events, even if there are some common patterns of variability within storms.[49–51]

CANOPY PROCESSES AND THEIR ISOTOPIC EFFECTS

Isotopic shifts in TF occurring with interception have typically been categorized as three factors—evaporation, exchange, and selection (Figure 1(b)–(d)).[52] Evaporation causes kinetic and equilibrium fractionation that vary with RH, and TF that undergoes evaporation is enriched in heavy isotopes and has decreased d (Figure 1(b)). Exchange entails equilibrium fractionation by liquid–vapor exchange when the two pools (vapor and liquid) are not at isotopic steady-state (isotopic values cease to change with further exchange, and the two pools are offset from each other by the constant fractionation factor). Precipitation and vapor δ_w in the canopy airspace will likely not be in steady-state with incoming precipitation δ_w, causing isotopic shifts in both vapor and liquid pools as they exchange water molecules (Figure 1(c)). The exchange effect can cause isotopic deviation in any direction, similar to the interaction of falling rain droplets with the ambient atmosphere.[48,51,53,54] Selection refers to deviations in TF that result from selective transmittance of temporally varying rainfall along varying canopy flowpaths precipitation with temporally fluctuating δ_w (Figure 1 (d)). For example, if precipitation δ_w at the end of an event is isotopically lighter than bulk precipitation and that ending precipitation is retained in the canopy, bulk TF from that event is isotopically heavier than precipitation. Like hillslope flow processes, spatiotemporal isotopic variations arise by selection from the routing of liquid water with temporally varying isotopic inputs along varying flowpaths (e.g., TF vs SF), buffered by mixing with different storage elements. While there is overlap in the

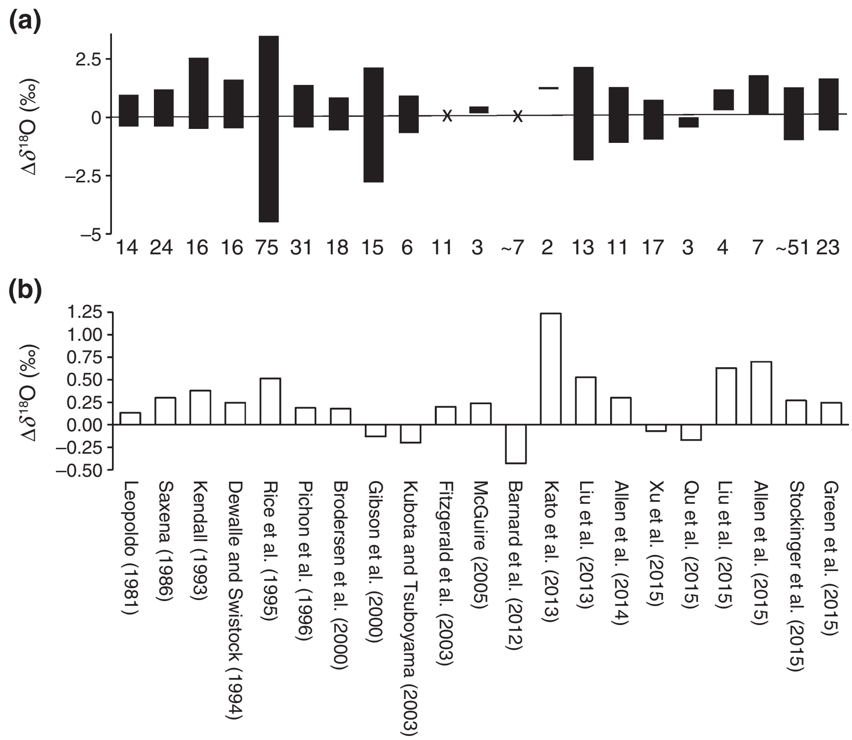

FIGURE 2 | Differences between $\delta^{18}O$ in throughfall and open precipitation (TF–OP): (a) range of single-event differences, and (b) study-mean differences. The number of measurement intervals (events) by study is between panels. Some values are arithmetic means and others are volume-weighted; see Table 1. An 'X' indicates data are not available.

processes represented by the terms evaporation, selection, and exchange, they are independent enough to be useful in categorizing the net effects of canopy interception processes.

Evaporation, exchange, and selection all occur in the canopy[46] and result in isotopic offsets of TF and SF from OP. While some within-canopy processes are similar to fractionation or mass flux processes affecting falling precipitation in the atmosphere, the within-canopy environment is different because it involves relatively small storage reservoirs with rapid turnover, effects of the canopy boundary layer on aerodynamic exchanges, and distinct temperature and humidity patterns. Wet-canopy evaporation generally occurs under high humidity dominated by equilibrium fractionation. Given the small storage reservoirs for intercepted precipitation and the dynamic nature of precipitation δ_w, isotopic exchange (Figure 1(c)) with vapor in the canopy airspace lagging intercepted water δ_w likely influences TF δ_w. Even with net evaporation, exchange could result in TF that is isotopically lighter than OP. Additionally, canopy storage composed of small reservoirs may evaporate completely, thus transmitting no fractionation signal to measured TF. Prior to any empirical studies, Gat and Tzur[52] hypothesized that fractionation by evaporation during storms would be low and that fractionation effects would be most prominent in the case of inter-storm carryover of partially evaporated canopy storage.

The physical mechanisms of interception evaporation are still not completely understood, and that uncertainty limits interpreting observed isotopic effects of rainfall interception (Table 1). Experimental data have revealed mismatches between interception models and energy, radiation, and mass balances in canopies,[55] and development of more general models will likely require more precise consideration of processes such as splash droplet formation[56] and the relative importance of radiation compared to advected heat.[57] Thus, notions of the factors controlling isotopic composition of TF should not be considered physical processes, but as suites of partially defined physical processes acting in concert.

Spatially Aggregated Temporal Variability in TF–OP δ_w Differences

Most interception studies using stable isotopes have measured TF–OP δ_w differences (Table 1), which vary among events in both magnitude and direction (Figure 2(a)). Of 22 such studies, 17 found that study-mean TF δ^{18}O was heavier than mean OP δ^{18}O, with several showing differences >0.5‰ (Table 1) and the global mean for studies with >10 sampling periods was 0.19‰ (Figure 2(b)). Temporally aggregated δ_w effects were smaller than those of individual events. Despite interception loss (i.e., net evaporation), studies often observed event-mean TF to be isotopically lighter than OP (Table 1). Both positive and negative event-mean TF–OP δ_w differences were observed in 13 of 18 studies, with the remaining five studies having small sample sizes and fewer than three events or seven weekly measurements. Not surprisingly, studies with more samples observed greater variation of single-event TF–OP δ_w differences; the greatest variability was observed in a study incorporating 75 measurement periods,[25] although the TF and OP collectors were 3 km apart, so spatial variability of OP δ_w may have played a part in the results.

Canopy δ_w effects depend on storm and pre-storm conditions. Larger TF–OP δ_w differences have been observed in events with lower OP amount,[31,35,40] duration,[31] or intensity.[24,36] Correlations between event interception loss and TF–OP δ_w differences have been weak[23,24,27,36,40] despite correlation between interception loss and intensity and amount.[58] Smaller storms tend to have a greater likelihood of TF that is isotopically lighter than OP,[23,35] just as individual events means are more likely than study means to have TF with lighter δ_w than OP (Figure 2(b)). Inter-event carryover of intra-canopy vapor[23] or residual storage[36,52] has greater effects on TF in small storms too. The ambient vapor δ_w, a residual signal from previous events or larger-scale processes, and its difference from OP δ_w is a strong predictor of TF–OP differences and fractionation.[22]

In dual isotope space, several studies have shown that TF, SF, and OP δ_w tend to fall along similar local MWLs with slopes near 8,[23,28,29,35,38] although one study found the TF slope to be well below that of OP.[31] Similar to TF–OP single-isotope differences, the *d* differences vary among events and studies.[31,37] Sometimes TF *d* exceeded OP *d*, attainable by disproportionate transmission of OP with relatively higher *d* (i.e., selection; Figure 1(d)) or by exchange with high-*d* vapor (Figure 1(c)), but not attainable by evaporation (Figure 1(b)).

Event and Inter-Event Patterns of δ_w Spatial Variability among Different Plots, between TF and SF, and among Collectors

The range of spatial variation in TF δ_w for events often exceeds the event-mean TF–OP δ_w difference (Table 1). Within single events, simultaneously positive and negative TF–OP δ_w differences have been commonly observed between plots,[23–25,27,37] between TF and SF,[27,29,36] or among individual collectors.[23,27,35,36,40] The range of δ_w between TF and SF collectors varied widely among studies (Figures 3 and 4). However, because variance is related to collector size, collection interval, and number of collectors,[40] comparison among studies is difficult. The greatest range (11.8‰ δ^{18}O) was in a study measuring individual events with 100 small (145 cm^2) collectors.[43]

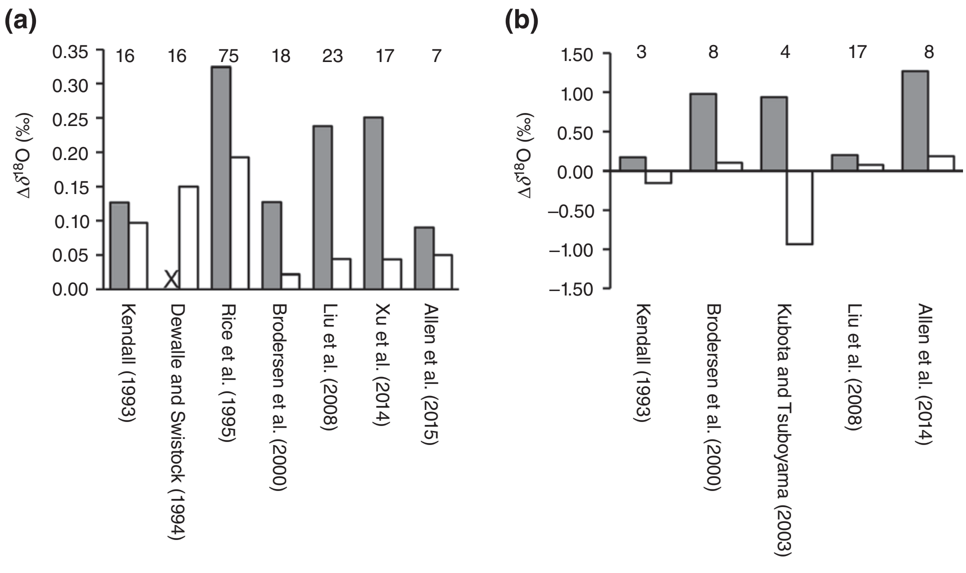

FIGURE 3 | Study-mean differences in δ^{18}O (a) among throughfall collectors within plots and (b) between throughfall and stemflow. Open bars are mean differences and shaded bars are mean absolute value of differences. An 'X' indicates data are not available. Numbers of intervals measured are indicated above the bars.

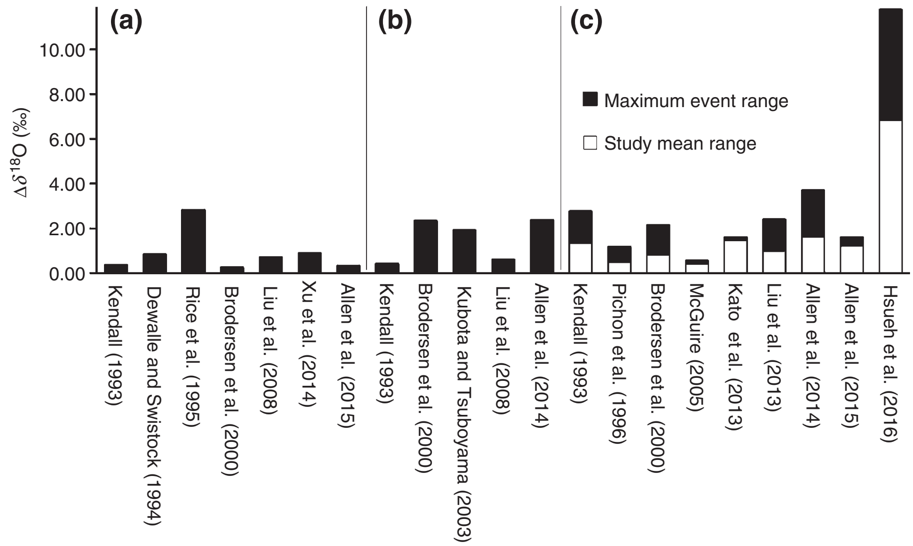

FIGURE 4 | Greatest individual-event ranges of $\delta^{18}O$ for each study: (a) between plot means in throughfall, (b) between throughfall and stemflow, and (c) among individual throughfall collectors; open bars indicate that mean spatial range across all events is also included.

Over multiple events, study-mean δ_w differences between plots, collectors, and TF–SF are substantially less than in single events (Table 1; Figure 4) due to unstable spatiotemporal patterns in canopy effects on δ_w.[27,40] Instability results in patterns from individual events to not aggregate into patterns at longer timescales, instead tending to cancel each other out and converge toward spatial homogeneity. Accordingly, effects of spatial variations are less significant to applications using temporally aggregated data. While Hsueh[43] noted some temporal persistence in spatial isotopic patterns, it was in a small sample of storms.

Several studies have shown that relatively denser canopies, either within or between stands, correspond with greater effects on δ_w of TF. In studies where TF was isotopically heavier than OP, denser stands had isotopically heavier TF than less dense stands.[23,24,31] Xu[37] observed that TF was isotopically lighter than OP, and that effect was also greater in denser forest. Studies have consistently shown a greater isotope effect in coniferous forests compared to broadleaf forests,[23–25,27,37] possibly related to their higher storage capacity.[59] At the sub-plot scale, findings have been similar, with greater isotope effects under denser areas of forest but not in a consistent direction of variation.[27,34]

The relationship between TF amount and δ_w differs at the collector and plot scales. Among plots, those with lower mean TF amount usually experience a greater isotope effect, whether enriched or depleted.[23,24,27,31,37] Within plots, variable patterns have been observed; Kato[34] observed both strong positive and negative correlations between TF amount and δ_w per event but further analysis of those data found no relationship when averaged across events. Other studies similarly found inconsistent relationships between TF amount and δ_w across events.[23,40,43]

While both OP δ_w and spatially aggregated TF δ_w generally fall on similar MWLs (section *Spatially Aggregated Temporal Variability in TF–OP δ_w Differences*), within single events spatial observations may constitute a line with a substantially different slope than OP[23,36,43] (Figure 1(b) and (d)). For individual events plotted in dual isotope space, studies have observed clustering of most points with a few strong outliers.[23,34,36,43] This clustering effect is consistent with the buffering effects of exchange (Figure 1(c)); in contrast, selection would result in variability along an event MWL, bounded by the input variability (Figure 1(d)).

Intra-Event δ_w Differences between TF and SF

A few studies have measured paired TF and OP δ_w at the sub-event timescale, whether by sequential time increments[28,32] or volumetric increments.[23,29,33,38] Incremental TF δ_w mostly tracks the temporal pattern of OP δ_w but with slightly dampened variability.[23,28,29,32,38] Temporal patterns of SF δ_w, in contrast, have been much more temporally dampened.[29,32] For example, data presented by Kubota and Tsuboyama[29] showed mean $\delta^{18}O$ ranges of sequential volumetric increments for individual events were 7.4‰ for OP, 7.2‰ for TF, and 3.4‰

for SF. Similar to event-level patterns, δ_w of incremental TF or SF has been observed to be either isotopically heavier or lighter than paired increments of OP.[23,29,32]

Because of greater likelihood of fractionation, attention has been directed toward TF–OP δ_w differences at the beginning and end of storms. Ikawa et al.[32] sampled synchronous increments of SF, TF, and OP throughout one large storm and observed that initial TF δ_w was enriched relative to concurrent precipitation. At the end of the event, SF continued for hours after precipitation stopped but remained isotopically similar to OP at the end of the storm. Kendall,[23] in contrast, observed TF to be enriched at the end of storms relative to OP.

Intra-event increments of OP, TF, and SF δ_w all tend to fall along MWLs of similar slope.[23,29,33,38] However, those slopes can be quite variable, ranging from 3 to 11.[23] Kubota and Tsuboyama[29] presented maximum, minimum, and mean from intra-event data; lines composed from those points showed the TF and OP MWL slopes were nearly identical. However, intra-event variations may not be well represented by an MWL because incremental variations are not always linear in dual isotope space[23] as some parts of storms may fall on evaporation lines (Figure 1(a)).

DISCUSSION OF FACTORS CONTROLLING ISOTOPIC COMPOSITION OF INTERCEPTION

Patterns in δ_w have led to varying published conclusions on the relative influences of evaporation, selection, and exchange on TF. Identifying the roles of these factors may aid in the development of predictive models, but there has rarely been sufficient data collected to draw strong conclusions. Here, we use the available evidence to examine the degree to which observed canopy isotope effects are attributable to each factor.

Discussion of Spatially Aggregated Temporal Variability in TF–OP δ_w Differences

Some investigators have attributed storm-total TF–OP δ_w differences to fractionation occurring with evaporation. While the relatively higher abundance of heavy isotopes and lower d in TF as compared to OP (Table 1) is consistent with evaporation effects (Figure 1(b)), this alone is not sufficient to conclude kinetic evaporation is important. For instance, even if evaporation causes TF to deviate from OP, along a slope <8, the resulting TF MWL across multiple events would not necessarily have a lower slope (Figure 1(b)). Furthermore, there are other observations that are not consistent with evaporative control on TF–OP δ_w differences. Most studies have also observed some events with net isotopic depletion despite net interception loss (Table 1). Generally investigations (e.g., Kendall[23]) have largely borne out the logic of Gat and Tzur[52] that evaporation plays a small role in storm-total TF–OP δ_w differences. However, the commonly observed study-mean positive TF–OP difference in δ_w may indicate that evaporation effects are consistent but small, adding up (exceeding typical analytical precision[60]) over longer periods of time yet overwhelmed at the event scale by selection and exchange.

Authors do not agree on which canopy processes cause selection effects, as evidenced by the many different notions of selection.[24,27,43,52] Simple enrichment of TF δ_w due to the selective canopy retention of the last and (often) most-depleted increment of OP was an early suggestion,[24] but this is too simple of an explanation because temporal patterns in OP δ_w are not sufficiently predictable, and there is no temporal stability in TF–OP differences.[23,36] The alternate assumption, that complex transmission patterns of TF and SF[61] coupled with highly variable intra-event δ_w of OP[62] lead to unpredictable effects of selection, is not well tested because it could cause such a large variety of isotopic deviations in any direction from OP (within the event mixing space; Figure 1(d)). Data that are seemingly consistent with evaporation, such as TF with a lower slope of the MWL than OP,[31] are also consistent with selection because of covariation of enrichment and d in OP.[49,51] Thus, predicting effects of selection requires both knowledge of OP δ_w at high frequency and also mixing and routing of water through the canopy.

Liquid–vapor exchange effects on TF δ_w are under-investigated. The one study that measured δ_w of both TF and vapor found that the liquid–vapor exchange effects overwhelmed those of evaporation.[22] Even without vapor measurements, others have concluded their results are consistent with exchange,[23,32] partially because of observations that TF can be enriched or depleted relative to OP. Non-steady-state conditions between liquid and vapor are probable, given the small vapor mass of the canopy airspace (e.g., a 20 m layer of air at 25°C saturates at ~0.5 mm of water) and that precipitation δ_w can vary rapidly within events (e.g., 4.6‰ $\delta^{18}O$ min^{-1} [62]). The greatest exchange effects likely occur in successive, rapidly moving showers with high saturation vapor pressure (i.e., large ambient vapor reservoir) and rapid variation in δ_w of both rainfall and vapor.[23]

With storm-total data, selection may not always be discernible from exchange because storm temporal variability is rarely known and likely plays a similar role in both exchange and selection. Similar variations in δ_w of TF–OP could be caused by either selection or exchange (Figure 1), although it has been reasoned that selection effects would be smaller.[27] The fact that smaller storms generally show larger isotope effects might indicate that: (1) evaporation is important because small storms have greater evaporation generally (although this conflicts with small storms also showing net depletion[23,37]); (2) exchange is important because the canopy airspace is dominated by antecedent vapor; or (3) selection is important because the ratio of canopy storage to event size is larger, increasing the likely magnitude of selection effects. Similarly, the lack of correlation between interception loss and TF–OP δ_w difference has been cited as evidence against control by evaporation.[24,27] However, it is unknown how much interception loss occurs by complete evaporation (no net isotopic effect except the exclusion of that water from contributing to TF) versus partial evaporation of stored water that eventually drips. Thus, developing mechanistic understanding of canopy interception effects on event TF–OP δ_w differences likely requires observations at finer scales.

Discussion of Spatial Variability at Event or Aggregated Time Scale

Greater interception loss in denser stands is generally attributable to greater canopy storage capacity,[58] but this does not necessarily relate to the common positive relationship between forest stand density and the magnitude of isotope effect (section *Event and Inter-Event Patterns of δw Spatial Variability among Different Stands, between TF and SF, and among Collectors*). Evaporation from larger storage would only yield more enriched TF δ_w if the storage were not fully evaporated. Aside from higher storage, denser canopies also decrease exchange with the atmosphere,[63] especially in broadleaf canopies,[64] with uncertain effects on isotopic exchange between liquid and vapor in the canopy space. Greater isotope effects in needle-leaf forests[23,24,27,37] may be due to aerodynamic differences or storage differences. Perhaps the best evidence against evaporation control over TF δ_w is that denser stands show larger TF–OP δ_w deviations in either direction (section *Event and Inter-Event Patterns of δw Spatial Variability among Different Stands, between TF and SF, and among Collectors*). Such observations suggest dominance of selection or exchange over spatial variations because evaporation alone could not yield TF that is isotopically lighter than OP.

The lack of temporal stability in intra-stand δ_w spatial patterns, despite relatively stable spatial patterns of TF amount,[36,40,43] suggests multiple possible interpretations of controlling processes on TF routing. At the sub-plot scale, variation in amount of TF among collectors or between TF and SF is likely due to canopy heterogeneity and lateral redistribution; good evidence of this is that TF in individual collectors can exceed OP.[46] Selection arising from differential routing and mixing with stored water would increase variability, especially when mixing with partially evaporated water or water from a previous event.[36,52] Thus, lack of temporal stability in spatial patterns of δ_w may support alternate conclusions that either flowpaths through the canopy are not as consistent as hydrometric data suggest they are, or that exchange and mixing with pre-event water is more common than has been assumed. Exchange with vapor is not likely responsible for spatial heterogeneity in TF δ_w, but is instead more likely to provide a homogenizing effect that may contribute to spatial smoothing of δ_w. However, exchange effects are likely relatively small.[27]

Discussion of Intra-Event Spatiotemporal Variability

The few studies that have measured intra-event temporal and spatial variability of TF δ_w are particularly useful for process examination. These investigations have revealed that SF has much greater liquid–liquid mixing or liquid–vapor exchange than does TF, as evidenced by damped and lagged in-storm variability in δ_w compared to TF or OP[29,32] The temporal smoothing in SF δ_w suggests that SF is a product of input OP mixing over many hours. This higher resolution has provided some evidence that evaporation and exchange effects on δ_w are greater at the beginning and end of events.[29,32] However, the experimental body is small and more incremental measurements are needed to resolve the relative effects of evaporation, exchange, and selection.

A VISION FOR FUTURE RESEARCH

While evaporation, selection, and exchange all occur, our current limited ability to separate the influences of each one hinders predictive applications of these concepts. The predictive success achieved with simultaneous measurement of $\delta^{18}O$ in liquid and vapor[22] shows that one path forward for estimating aggregated effects is to collect more such data and use it to model exchange more generally. However, generalizing the understanding of selection may be difficult because selection effects are dependent on canopy structure, flowpaths through the canopy, and variable isotopic composition of rainfall. Recent work has made advances in describing canopy transmission related to weather patterns[61] and how weather patterns control intra-event variations in δ_w,[49–51] and incorporating these factors may be necessary for an efficient model of selection. However, some model of flow routing would also be needed, and there has been little progress in this area.

Given that interception δ_w signals do not always cause large errors in isotope tracer applications (Box 1) or propagate through to other parts of the hydrologic system (Box 2), the variability in TF δ_w may be most useful for resolving the specific processes occurring in the canopy. Accordingly, terms such as 'selection' that describe net effects on TF δ_w rather than the processes that generate those effects should be revised toward terms that describe basic processes such as evaporation and water or solute transport in the canopy.

Parallels between water flows in the canopy and the subsurface may allow us to adopt analogous methods for new research to help illuminate interception processes. Like watersheds, canopies are also variable retention filters generating flow from a variety of pathways and reservoirs. For some applications, hydrometric analyses and simple lumped models are appropriate, but to address the causes and consequences of spatiotemporally varying water and solute transport in the canopy, more detailed representation of canopy processes is needed. Only then can residence times and flowpaths for water and solutes be resolved. As in watershed research, stable isotopes are a potential tool for bridging experimental findings and model representations because they provide insight into the flow, storage, and mixing mechanisms.

How Does Water Mix in the Canopy?

We do not know how water moves on the surfaces of various canopy components. For example, is water flow on leaves and stems dominated by piston flow, well-mixed turbulent flow, or bypass flow? The exchanges between bark, leaves, and TF need further clarification because of their consequences on residence times and solute budgets. Patterns of variability, temporal persistence, and the apparent role of antecedent wetness on solute transport in TF and SF provide some insights,[9] but variability of chemical constituents in TF and SF is different from variability of quantity[46] or δ_w. Consequently, the current understanding of canopy flow processes is insufficient for generalizing these processes (e.g., which flowpaths are associated with chemical constituents that require reaction time rather than just flushing).

BOX 1

IMPORTANCE OF THROUGHFALL VERSUS RAINFALL FOR TRACER APPLICATIONS

Interception effects on δ_w could affect interpretation of tracer applications. With direct statistical comparison of TF and OP δ_w (e.g., comparing dual isotope regression slopes or *T* tests of means), there is great risk of a Type II error (conclude no effect when one exists) because of low sample sizes and statistical properties of TF isotopic spatiotemporal variability.[40] Accordingly, authors have sometimes concluded no substantial OP–TF δ_w difference[28,42] because of inconsistent spatial variability among events. However, mean OP–TF δ_w differences (Figure 2(b)) typically exceed analytical errors.[60] Relevance of the canopy effect is application-specific, in part because of a tendency for temporal and spatial variations to be reduced by integration across larger spatial and temporal scales (Figures 2–4). At the event or subevent scale, Kubota and Tsuboyama[29] showed that using OP instead of TF in a watershed model can result in a 5–10% difference in estimated event water contributions to stream flow. At weekly or longer scales, Stockinger et al.,[41] showed that incorporating TF–OP δ_w difference in models could affect conclusions on watershed transit mechanisms. Thus, even though accumulation across multiple events or collectors reduces variability, systematic offsets usually occur and have impacts. While there has been little investigation of relevance of interception effects on conclusions regarding plant water uptake, systematic offsets by interception could affect interpretation of plant water source partitioning[78] inferred by, for example, xylem water or $\delta^{18}O$ variations in wood.

While it is known that canopy storage is not a simple fill-and-spill reservoir or a batch reactor of biogeochemical processes, more detailed investigation is needed for mechanistic understanding. High temporal resolution measurements of paired OP, TF, and SF δ_w would be useful in identifying differences in the relative mixing along flowpaths. The few studies that have made relevant measurements showing how different components mixed with stored water[29,32,36] have yielded insights that show the potential of isotopic applications (section *Discussion of Intra-Event Spatiotemporal Variability*). Further analysis, e.g., transfer function analysis (previously attempted using

BOX 2

PROPAGATION OF CANOPY ISOTOPE EFFECTS TO OTHER HYDROLOGIC SYSTEM COMPONENTS

Variability of TF and SF amount is of interest because of consequent effects on soil moisture patterns,[79] especially with respect to stemflow, where water may preferentially contribute to rapid infiltration or plant-available water.[5,6] Soil storage and subsurface flow generally buffer isotopic temporal and spatial variability caused by interception.[27,80] However, in systems where stemflow is high (e.g., >30% of OP[81]), SF may transmit rapidly to the subsurface and streamflow. While there is no specific evidence that interception effects are responsible for complex isotopic patterns of soil moisture and plant water uptake, SF could cause patterns of isotopic variation along roots that contrast with the surrounding soil.

The net fractionation effect with interception must be mirrored in fractionation of water evaporated to the atmosphere. The role of interception loss in continental scale vapor *d* is unclear,[20,82] and if TF–OP δ_w differences are primarily a result of spatiotemporal redistribution (i.e., not fractionation), effects on the δ_w of ambient vapor would be small.[44] However, studies have shown long-term offsets of δ_w in TF from OP (section *Spatially Aggregated Temporal Variability in TF–OP* δ_w *Differences*), which entails a corresponding atmospheric vapor effect. Continental patterns of *d* have been speculatively attributed to interception loss.[82] Ultimately, the magnitude of canopy fractionation effects may be small compared to other factors, which limits the ability to distinguish specific interception effects on vapor.[20]

hydrometric data[65]), could be used to calculate the transit times along these flowpaths. This novel type of characterization of the canopy could facilitate upscaling of canopy hydrology and biogeochemistry to the watershed scale.

How Generalizable Is the Distribution of Flowpaths in the Canopy?

Although storage is often treated in a spatially integrated way, TF and SF travel to the forest floor by a diversity of flowpaths with varying storage interactions, including thin films and flows on hydrophilic surfaces, droplets on hydrophobic surfaces, and water absorbed in bark or epiphytes. Much has been written about this diversity,[10,59,66,67] illustrating the need to consider spatially explicit storage and routing. However, to progress, we need to consider how generalizable these patterns are.

In describing the variation of flowpaths through the canopy, typically only TF and SF have been described separately. However, spatial variation in δ_w of TF suggests a continuum of variability (section *Event and Inter-Event Patterns of* δ_w *Spatial Variability among Different Stands, between TF and SF, and among Collectors*) between TF and SF. For example, TF at some locations is more isotopically similar to SF than other TF,[27,36] presumably due to more time spent in the canopy and interaction with different reservoirs. With extensive spatial sampling,[23,27,34,36,43] the large spectrum of TF spatial δ_w variations show the diversity of OP mixtures or mass-exchanges processes that water underwent. Overall, binary classification of TF and SF as distinct alternate flowpaths may be useful for some application but not others, but a generalized description of flowpaths through canopies should probably subsume the full range of intermediate cases.

Extensive sampling to support identification of spatial distribution of both hydraulic and particle transit times would be a path toward understanding generality of flowpaths. Specifically, temporal δ_w increments collected simultaneously at multiple locations in plots would be instructive; the volumetric increments that have often been used in TF studies[29,33,38] create a challenge for relating input to output δ_w because volumetric differences between OP and TF obscure variability and mask temporal effects. More easily, some aspects of the spatial heterogeneity in flowpaths can be seen through differences in the propagation of a pre-event storage signal.[36] For example, if two consecutive storms occurred where isotopic composition varied between events substantially but not within, TF that interacts with stored moisture could be distinguished from that which behaves like bypass flow.

What Is the Role of Rain Splash in TF and Evaporation?

Murakami[56] argued that the majority of interception evaporation likely occurs by rapid evaporation of micro-droplets created by splash after rain impacts the canopy, with rates of micro-droplet evaporation potentially accelerated by shear stress between falling droplets and air.[68] The droplet size of OP is generally between 0.1 and 5 mm,[69] which upon impact with the canopy may yield droplets that are an order of magnitude smaller (median diameters 0.01–1 mm[68]). Despite much speculation, there remains considerable uncertainty about the importance of micro-droplet formation, subsequent evaporation, and contribution to TF.

Stable isotopes provide a way to resolve the importance of splash droplets by comparing δ_w of OP, TF, and SF to δ_w of canopy space vapor by taking advantage of the fact that smaller droplets in the canopy space reach isotopic steady-state with ambient vapor more rapidly. For example, equilibration occurs in 5.1 m for a 100 μm droplet compared to thousands of meters for typical rain drops.[51,54] Stored water in bark or surface films would be expected to exchange even more slowly. Resolving this phenomenon would be possible by new sampling schemes, for example, sampling vapor and water at high spatial density while accounting for drop-size variation.

How Can We Integrate Canopy Hydrology into Watershed Hydrology?

Interception is often considered synonymous with 'interception loss'—that is, evaporation from wet canopies. Although wet-canopy evaporation probably has the greatest effect on stormflow,[70] some have recognized the potential for spatiotemporal moisture redistribution by canopies[1,2,15,46] to affect flow generation in hillslopes[71,72] and vegetation water use.[5,6,8] Tracers are playing a role in linking these processes,[73] but, so far the potential of isotope tracers in canopy systems has not been well developed. An important barrier to integrating canopy effects on flow routing into watershed hydrology models is that progress has been mostly limited to empirical evidence of patterns rather than theoretical developments to describe physical processes.

The physics of routing flows through canopies needs theoretical development in a way that will be useful in watershed models. In porous media, mass, momentum, and energy balance equations have connected basic physics to practical models allowing for scaling up to watersheds.[74] However, canopy effects have been omitted from those efforts. The physics of precipitation routing through canopies are different from soils, with respect to roles of capillarity versus gravitational flow, laminar versus turbulent flow, and the specifics of two-phase flow (in particular, drops in free fall through vapor). The concept of a canopy matrix analogous to the soil matrix may be not tenable, which is apparent in the shortcomings of defining TF output as a simple function of storage and input (i.e., drip equations[65]). Even some of the mechanistic developments regarding TF generation[12,46,75,76] have not been integrated into commonly used empirical drip equations.[65] There are challenges in obtaining necessary data to generalize canopy flow generation behavior because canopy architecture lends organization to flow with a dizzying range of vegetation characteristics to consider.[46,59] Nonetheless, isotopes are an effective tool for both examining processes and describing complex distributions of spatiotemporal variability.

Those studying canopy interception have the opportunity to use tracers to complement hydrometric data. Beyond providing a means to examine physical processes, the attraction of isotopic tracers as a tool is that they offer promise in developing datasets that transcend scales. Signatures of fine-scale processes such as splash droplet formation,[68] concentrated and rapid flow at drip tips on waxy leaves,[66] and retention in epiphytes[59] all have specific but diverging consequences for δ_w of TF and SF. Sivapalan[77] suggested that successful modeling of watershed hydrology depends upon modeling flow behavior at both fine and large scales because the organization of watershed elements and feedbacks among them contribute to large-scale behavior that is more than a sum of small-scale parts. Identifying the importance of flowpaths through the canopy, and thus the models necessary to represent them, can be aided by isotopic tracers in canopy hydrology much as in hillslopes and watersheds.

CONCLUSION

Stable isotope tracers can inform a new understanding of TF or SF generation. However, examination of bulk event differences between isotopic composition of TF and rainfall is unlikely to lead to sufficient mechanistic understanding of interception effects necessary to develop predictive models of net precipitation isotopic composition. Interception-isotope effects result from isotopic transience in ambient vapor and precipitation, coupled with flow along different canopy pathways and equilibrium and kinetic fractionation processes associated with liquid–vapor exchanges. Although these processes all occur, the net effects of their conditionally varying influences are useful evidence of the relative effects of selection, evaporation, and exchange. The research community can benefit by going beyond attribution of canopy isotope effects to oversimplified notions of these processes.

The processes that control TF and SF isotopic differences from precipitation occur at varying spatial and temporal scales. Isotopic differences between TF and OP accumulated over extended periods across multiple events are generally small and positive, consistent with expectations associated with evaporation. However, for individual events, differences vary in magnitude and direction in ways that could only be explained by exchange or selective transmittance of temporally varying rainfall. Among multiple collectors in individual events, isotopic composition is highly heterogeneous, attributable mainly to selection that arises from differences in flowpaths and mixing with storage, similar to controls over isotopic variability in larger-scale hydrologic systems (e.g., watersheds).

Finer resolution of measurements is needed for process-level inferences regarding the evaporation, mass exchange, and transport of water through the canopy. The few studies that focused on fine-scale spatial and temporal isotopic variations identified patterns that show heterogeneity in mixing and transport processes. More detailed experiments could better reveal how water moves through flowpaths and storage reservoirs in the canopy, much like isotopes have helped propel our understanding of flowpaths and residence times in watersheds.

ACKNOWLEDGMENTS

We thank Kevin McGuire, WIREs Water editors, and three anonymous reviewers for helpful comments on the manuscript, as well as Michael Stockinger, Mark Green, and Kevin McGuire for sharing data with us. Helpful discussions early on with Barbara Bond and Friso Holwerda helped lead to this work.

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