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Stable water isotopes suggest sub-canopy water recycling in a northern forested catchment

Mark B. Green,[1,2]* Bethany K. Laursen,[3] John L. Campbell,[2] Kevin J. McGuire[4] and Eric P. Kelsey[1,5,6]

[1] *Center for the Environment, Plymouth State University, Plymouth, NH, 03264, USA*
[2] *Northern Research Station, USDA Forest Service, Durham, NH, 03824, USA*
[3] *Department of Forest and Wildlife Ecology, University of Wisconsin, Madison, WI, 53706, USA*
[4] *Virginia Water Resources Research Center and Department of Forest Resources and Environmental Conservation, Virginia Tech, Blacksburg, VA, 24061, USA*
[5] *Department of Atmospheric Science and Chemistry, Plymouth State University, Plymouth, NH, 03264, USA*
[6] *Mount Washington Observatory, North Conway, NH, 03860, USA*

Abstract:

Stable water isotopes provide a means of tracing many hydrologic processes, including poorly understood dynamics like soil water interactions with the atmosphere. We present a four-year dataset of biweekly water isotope samples from eight fluxes and stores in a headwater catchment at the Hubbard Brook Experimental Forest, New Hampshire, USA. We use Dansgaard's deuterium excess (*d*) parameter to infer hydrologic processes that cause stable water isotope fractionation. Although we expected to observe a decrease in *d* from precipitation to soil water because of evaporation, instead we observed an increase, which suggests sub-canopy water vapour recycling (evapotranspiration and then re-condensation). However, the underlying mechanisms and spatial dynamics remain uncertain. The apparent recycling is most evident in the growing season; weak evidence suggests a similar process in the dormant season. Sub-canopy water recycling is a novel hydrologic process that should have implications for micro-meteorology and habitat provided by the forest sub-canopy environment. Copyright © 2015 John Wiley & Sons, Ltd.

KEY WORDS water isotopes; deuterium excess; temperate forest; water recycling; evaporation; transpiration; Hubbard Brook

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INTRODUCTION

Stable water isotopes have been used extensively to trace hydrologic dynamics in catchments. Assuming conservative transport, water isotopes have improved our understanding of groundwater recharge (Scanlon *et al.*, 2002), snowmelt dynamics (McGlynn *et al.*, 1999; Laudon *et al.*, 2002), streamflow generation (Sklash and Farvolden, 1979; Shanley *et al.*, 2002), and solute transport through catchments (Hill, 1993; Asano *et al.*, 2006; McGuire and McDonnell, 2006). Similarly, the water travel time through a catchment is often calculated using water isotopes of precipitation and streamflow (Hooper and Shoemaker, 1986; Clark and Fritz, 1997; DeWalle *et al.*, 1997; McGuire *et al.*, 2002; St. Amour *et al.*, 2005; Kirchner *et al.*, 2010).

Other isotopic studies have traced non-equilibrium (kinetic) phase changes that fractionate heavy water isotopes from light ones, such as evaporation and condensation (Clark and Fritz, 1997). The non-equilibrium fractionation because of evaporation has enabled the partitioning of evapotranspiration (ET) into its individual components (i.e. evaporation and transpiration) in certain catchments. This method is based on the knowledge that transpiration does not affect the isotopic composition of soil water, whereas an evaporating soil moisture flux is depleted in ^{18}O and ^{2}H (D), leaving the residual water enriched in the heavier isotopes (Moreira *et al.*, 1997; Twining *et al.*, 2006; Sutanto *et al.*, 2014). This approach was initially used in lake evaporation studies (Gonfiantini, 1986) and has now been applied to a diversity of terrestrial ecosystems (e.g. Wang and Yakir, 2000; Ferretti *et al.*, 2003; Barth *et al.*, 2007; Rothfuss *et al.*, 2010), providing insight into the relative magnitude of different near-surface water and energy fluxes (Jasechko *et al.*, 2013).

Deuterium excess (*d*) provides a useful metric to gain additional insight into fractionating processes. The larger atomic mass of ^{18}O than D allows quantification of water movement through non-equilibrium phase changes. The atomic mass difference results in slightly faster fractionation of D relative to ^{18}O. This dynamic can be quantified by calculating *d*, which was defined by Dansgaard (1964) as $d = \delta D - 8(\delta^{18}O)$. The δD and $\delta^{18}O$ isotope ratios for

*Correspondence to: Green Mark, Center for the Environment, Plymouth State University.
E-mail: mbgreen@plymouth.edu

precipitation worldwide define the global meteoric water line (GMWL) and have a *d* of +10‰ (Craig, 1961). The meteoric water line for a specific location, referred to as the local meteoric water line (LMWL), may differ from the GMWL because of kinetic and equilibrium processes that effect the isotopic composition of water vapour that is the source of precipitation (Clark and Fritz, 1997). Water lines have been used to provide evidence of evaporation, because residual water subject to evaporation plots below the LMWL (Dansgaard, 1964; Clark and Fritz, 1997; Gibson and Edwards, 2002). Alternatively, *d* provides a single number for a water source that provides evidence of evaporation or other non-equilibrium phase changes (Dansgaard, 1964). Water condensed at equilibrium—the common condition for meteoric precipitation—retains the *d* of its source vapour, a memory of the kinetic evaporation it has experienced (Clark and Fritz, 1997).

Beyond tracing non-equilibrium phase changes, *d* can be used to trace mixing processes. For example, *d* has been used to identify the vapour sources of various meteoric waters (Lachniet and Patterson, 2002; Cui *et al.*, 2009; Lai and Ehleringer, 2010; Welp *et al.*, 2012). The amount of recycled water in water vapour can be quantified, with higher *d* values indicating enhanced moisture recycling (Gat and Matsui, 1991; Machavaram and Krishnamurthy, 1995; Gat, 1996; Zhang *et al.*, 2010). When different catchment source waters mix, *d* can also be used as a tracer of streamflow generation and to determine water residence times (Lee *et al.*, 2007; Kabeya *et al.*, 2007).

Here, we present results from a four-year study of stable water isotopes collected at the Hubbard Brook Experimental Forest (HBEF) in central New Hampshire, USA. We measured water isotopes from eight different sources at the HBEF to explore isotopic patterns that might indicate the magnitude of evaporation in this catchment. Contrary to our expectation of detecting evaporation along water transport pathways, we found patterns consistent with water recycling in the sub-canopy environment.

METHODS

Site description

This research was conducted at the 3160-ha HBEF located in the White Mountains of New Hampshire, USA (43°57′N; 71°42′N; Figure 1). The HBEF has nine gaged research catchments, four of which have been manipulated for long-term experiments (Likens, 2013). This study occurred in the hydrologic reference watershed (W3), a small headwater stream that drains 42.4 ha. The catchment has a south-facing aspect (S23°W) with a slope of 12° and an elevation range of 527–732 m. The climate is humid continental: average annual relative humidity is 88% and air temperate is 6 °C with an average monthly range of -8 °C in January to 18 °C July (Bailey *et al.*, 2003). On average, precipitation is distributed uniformly throughout the year with approximately 30% falling as snow. A snowpack usually persists from late December until mid-April, reaching a peak depth in March (average annual maximum depth of 72 cm or 19 cm snow water equivalent; Campbell *et al.*, 2010).

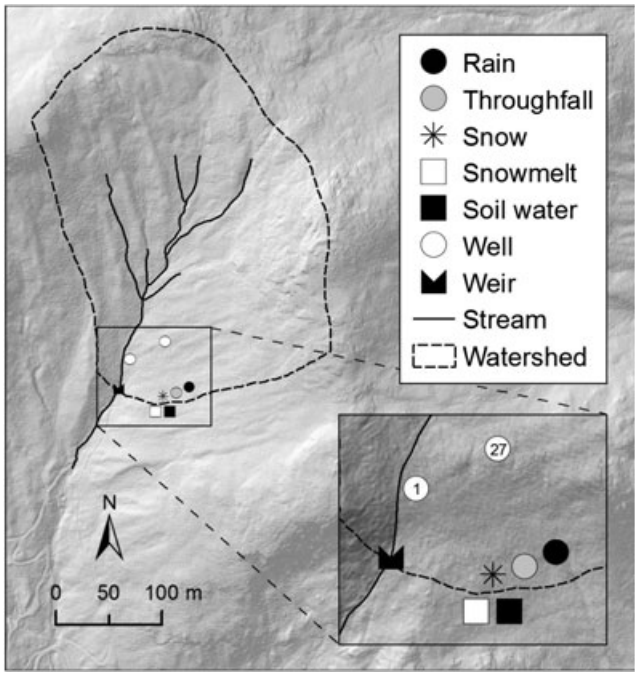

Figure 1. Map of Watershed 3 at the Hubbard Brook Experimental Forest and the location of water sampling sites for this study

The forest type in W3 is northern hardwood, consisting primarily of American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.), and yellow birch (*Betula alleghaniensis* Britt.). Leaf area index at HBEF is approximately 6 in the reference catchments with an elevation gradient from approximately LAI of 8 at 500 m to LAI of 4 at 700 m (Rhoads *et al.*, 2002; Fahey *et al.*, 2005). Interannual variation of mean LAI in the reference catchments ranges from around 6 up to 7, excluding deviations because of large disturbances (Battles *et al.*, 2013). The W3 catchment and much of the HBEF was harvested between 1909 and 1917, and the second-growth forest has been affected by some natural disturbances, most notably the hurricane of 1938 and ice storm of 1998. Soils in W3 are mostly well-drained Spodosols (Typic Haplorthods) with a thick (3–15 cm) organic layer at the surface that is highly permeable (Bailey *et al.*, 2014). Bedrock is sillimanite-grade pelitic schist and calc-silicate granulite of the Rangeley Formation and although highly variable, overlain by glacial drift with a solum thickness of 0.5 m. The bedrock is thought to be water-tight, with negligible catchment groundwater losses (Likens, 2013).

Many previous studies have focused on the hydrology of HBEF catchments. Streamflow averages 830 mm annually and has a strong seasonal pattern with highest flows typically during the period of snowmelt runoff. Assuming no change in interannual storage, discharge is 63% of annual precipitation, indicating that ET comprises the remaining 37%. The partitioning of ET is not well understood. At HBEF, estimates of interception losses from the canopy have ranged from 11 to 18% of incident precipitation (Leonard, 1961; Lovett *et al.*, 1996). Transpiration is presumed to be the dominant fraction of ET at HBEF (Federer and Lash, 1978), with most evidence from a forest harvesting experiment (Hornbeck *et al.*, 1997). The clear-felling and herbicide application for three years at one HBEF catchment increased water yield by 41%, which translates to a 71% reduction in ET (Hornbeck *et al.*, 1997). This can be interpreted as transpiration composing that full 71% of ET and the remaining 29% being evaporation from the canopy and soil. Subsurface water storage includes an unsaturated zone of approximately 1 m depth, with incursions of a water table depending on the hydropedological context (Bailey *et al.*, 2014; Gannon *et al.*, 2014). Streamflow generation at HBEF is primarily by displacement of stored 'old' water (Hooper and Shoemaker, 1986) that varies in age from weeks to years based on dynamic subsurface residence time modelling (Benettin *et al.*, 2015). Thresholds in subsurface storage control streamflow generation (Detty and McGuire, 2010b).

Water sampling

Water samples from various sources were collected bi-weekly throughout the year during October 2006 to October 2010 (Figure 1). Samples of precipitation, snowmelt, soil water, and stream water were collected over the entire four-year period. Throughfall and snow pack sampling was discontinued after two years, and groundwater sampling began in the second year and continued through the end of the monitoring period.

Precipitation samples were collected in an existing rain gage clearing at an elevation of 564 m. Precipitation collectors consisted of 15 cm diameter by 50 cm long PVC pipes lined with polyethylene collection bags. The collectors were mounted on vertical stakes 1.5 m above the ground surface. When precipitation fell as rain, mineral oil was added to the bags to minimize evaporation. To prevent contamination by the mineral oil, samples were obtained by cutting a hole in the bottom of the bag, allowing water to drain into the sample vial. When precipitation fell as snow, samples were melted at room temperature in a closed plastic bag after collection, and then immediately poured into sample vials. Throughfall sample collection was identical to precipitation, with the exception that a composite sample was obtained from 6 collectors randomly located under the forest canopy. The greater number of throughfall collectors was needed to better homogenize the spatial variability caused by the forest canopy.

Snowpack samples were collected by coring the entire snowpack with a bevelled, PVC tube. Snow cores were placed in plastic bags, and as with snow throughfall and precipitation, were melted at room temperature before decanting into sample vials. Samples of water draining from the bottom of the snowpack and soil were collected with lysimeters (1.064 m^2) installed near the rain gage clearing. As described by Campbell *et al.* (2007), the lysimeters consisted of heavy-duty (6 mm) PVC trays that drain by gravity through a PVC pipe to an underground storage container. The bottom of the lysimeter is impermeable and no roots bridged the soil in the lysimeter and the surrounding soil, thus the lysimeter soil was not directly hydrologically connected to the surrounding soil or the groundwater. The water storage container was insulated to prevent the drainage water from freezing. Soil lysimeters were installed in the soil at a depth of 10 cm, whereas snow lysimeters were placed directly on the surface of the forest floor. Both soil water and snowpack meltwater samples consisted of a composite sample from three lysimeters.

Groundwater was collected from two wells (Wells 1 and 27) in W3 that are part of a network described by Detty and McGuire (2010a). The wells consist of 3 cm diameter PVC pipe, with a 30 cm slotted screen at the base, and were installed to a depth of about 10 cm into C horizon of the soil (Well 1 is 88 cm and well 27 is 71 cm deep). Groundwater was collected from each well and passed through a 0.45 μm nylon membrane to remove sediment. Well 27 is located directly upslope from the stream at an elevation of 565 m whereas Well 1 is adjacent to the stream at an elevation of 535 m. Stream water samples were collected at the W3 outlet, just above the weir, about 50 m downstream from Well 1.

All water samples were stored in 20 mL glass vials that were completely filled with sample water and sealed with caps that contained plastic conical inserts to remove headspace and prevent evaporation. The caps of the vials were then dipped in paraffin wax and placed in the dark at room temperature until analysis.

Laboratory analysis

Isotopic results are reported in the standard δ notation in parts per thousand (‰) relative to Vienna Standard Mean Ocean Water (VSMOW):

$$\delta\,(‰) \;=\; (R_{SAMPLE} - R_{VSMOW})/R_{VSMOW} \text{x } 1000,$$

where R is the $^{18}O/^{16}O$ or D/H ratio of sample water or VSMOW. Oxygen isotopes of water were initially

determined using the CO_2-H_2O equilibration method (precision of 0.1‰) and hydrogen isotopes with the zinc reduction method (precision of 0.4‰) using a mass spectrometer following Coleman *et al.* (1982). After November 2008, the isotopic composition of water samples was measured using cavity ring-down laser spectroscopy as described by Lis *et al.* (2008) with an analytical precision of 0.1‰ for oxygen isotopes and 0.8‰ for hydrogen isotopes. A subset of 5 samples was run using both methods and showed a median difference of -3% and 5% for D and ^{18}O (-1.9 and 0.7‰) respectively. The analytical uncertainty of *d*, calculated as, $d = \sqrt{u(D)^2 + u(^{18}O)^2}$, was 0.41‰ for the initial method and 0.81‰ for the cavity ring-down method.

Data analysis methods

Seasonal differences for all water sources were evaluated by grouping data according to the dormant season and growing season as defined by the long-term average annual leaf-on/leaf-off dates measured at Hubbard Brook (October 19-May 7 for the dormant season and May 8-October 18 for the growing season; Richardson *et al.*, 2006).

The median water isotopic composition of the various water sources was compared with the LMWL in order to see the deviation of each source from precipitation. The LMWL was determined via least squares regression on all precipitation samples.

Changes in median *d* along the typical hydrologic flow pathway were investigated with a series of Mann-Whitney rank sum tests. These pathways were: precipitation to throughfall to soil water to shallow groundwater to streamwater for the growing season, and precipitation to throughfall to snow to soil water to shallow groundwater to streamwater for the dormant season. We compared adjacent water sources (e.g. throughfall and soil water, soil water and groundwater, groundwater, and streamwater) as well as non-adjacent sources (e.g. precipitation and stream water), which enabled statistical evaluation of both incremental and cumulative changes in *d*. Soil water may receive water from multiple sources; thus, we define the hydrologic 'input' to soil as precipitation/throughfall or snowmelt when a snowpack was present. Throughfall collection was discontinued after 2 years because the isotopic composition was not significantly different than precipitation according to a Mann–Whitney rank sum test ($n = 46$; 41%, and 62% of sample pairs showed an increase in δD and $\delta^{18}O$ of throughfall compared with precipitation respectively; $p = 0.729$ and $p = 0.646$ for δD and $\delta^{18}O$ respectively). Thereafter, precipitation was used as the input instead of throughfall. All tests were performed at the $\alpha = 0.1$ confidence level. It should be noted that the differences between these different water sources was used to infer where fractionation was occurring along typical flow paths.

RESULTS

Temporal variation of water isotopes

The $\delta^{18}O$ of precipitation showed substantial variation across years, exhibiting seasonal high values in the summer and low values in the winter, with some synoptic deviations (Figure 2a). The variation in snowpack and throughfall $\delta^{18}O$ was similar to precipitation, although $\delta^{18}O$ in throughfall was lower than precipitation during the summer of 2008. The seasonal cycling of $\delta^{18}O$ became more clear in soil water and snowmelt (Figure 2b), and even more clear in the shallow groundwater (Figure 2c) and streamwater (Figure 2d). Thus, the synoptic and seasonal amplitude of the $\delta^{18}O$ water input time series became increasingly damped as it was transported to streamwater. The same temporal patterns were apparent in δD data; thus, we only describe $\delta^{18}O$. The *d* values of precipitation and throughfall showed minimal seasonality and more stochastic variation than $\delta^{18}O$, ranging from −10 to 20‰ (Figure 3a). The temporal variation of other water source *d* demonstrated similar stochasticity, with some longer-lived deviations from typical values (Figures 3b–3d). For example, well

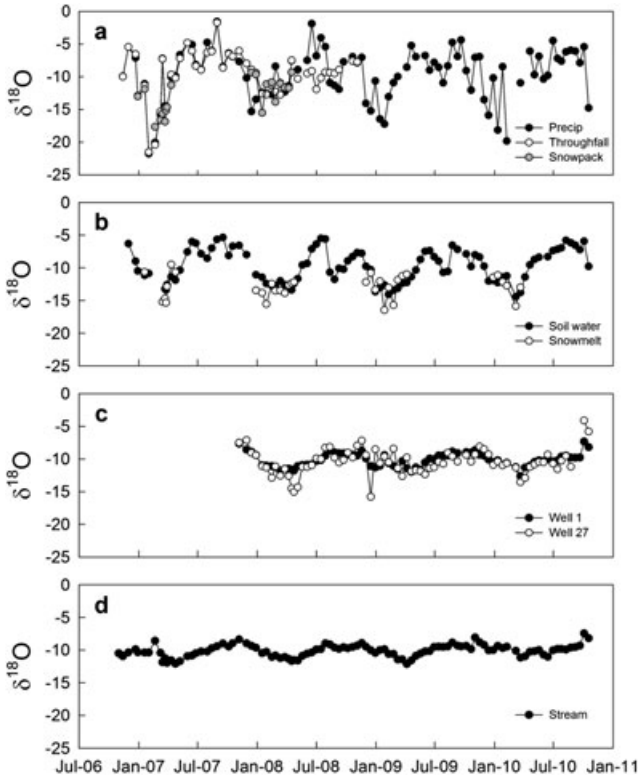

Figure 2. The time series of $\delta^{18}O$ in (a) precipitation, throughfall, and snowpack; 5 (b) soil water and snowmelt; (c) shallow groundwater; and (d) streamwater

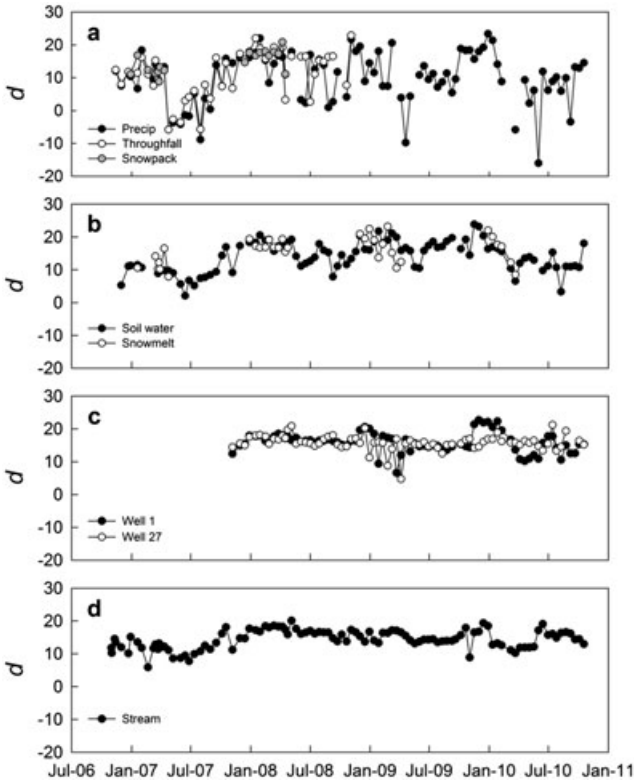

Figure 3. The time series of d (‰) in (a) precipitation, throughfall, and snowpack; (b) soil water and snowmelt; (c) shallow groundwater; and (d) streamwater

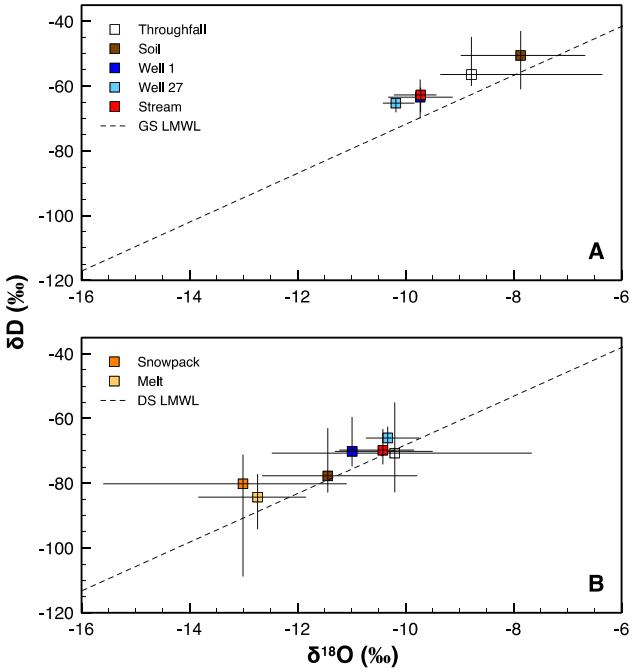

Figure 4. The seasonal LMWL with median and inter-quartile range of isotopic composition of different water sources showing (a) growing season and (b) dormant season

water during the winter of 2009 showed large changes from sampling period to sampling period.

Source water lines

The annual LMWL was $\delta D = 7.3(\delta^{18}O) + 3.36$, with a growing season water line of $\delta D = 7.56(\delta^{18}O) + 3.79$ (Figure 4) and a dormant season water line of $\delta D = 7.52$ $(\delta^{18}O) + 7.05$. When the median values from water sources were plotted separated by growing and dormant season, distinct seasonal differences between water sources emerge. Growing season throughfall, soil water, shallow groundwater, and streamwater all plot above the LMWL and are all higher than dormant season isotopic values (Figure 4a). Similar to the time series (Figure 2), damped variability in the groundwater and streamwater is apparent in Figure 4. The dormant season water sources all plot at or above the LMWL, with snow pack and melt showing the greatest deviation. However, the dormant season waters show much more variation for each water source, and thus, the dormant season waters were not clearly located off of the LMWL.

Isotopic change along flow paths

The $\delta^{18}O$, δD, and d changed along the catchment water transport pathway during the growing season more than the dormant season (Figure 5). Growing season precipitation, throughfall, and soil water showed considerable variation in $\delta^{18}O$, δD, and d compared with shallow groundwater and streamwater. We tested the statistical significance of changes in median d using a series of Mann–Whitney tests along the flow paths (Table I). The growing season precipitation and throughfall input was significantly different than soil water (2.24‰ increase of d, $p < 0.001$). The dormant season $\delta^{18}O$, δD, and d all showed dampening of variability along the flow path; however, the change of median d values did not significantly change unless distant parts of the flow path were compared (3.04‰ increase of d, $p = 0.057$). Analysis of both seasons together demonstrates the incremental change in d from precipitation to soil water (2.24‰ increase of d, $p = 0.023$), and then soil water to shallow groundwater (well 27 showed a 1.29‰ increase of d, $p = 0.039$). The difference between shallow groundwater and streamwater was not significantly different. Change of d along the precipitation–soil–groundwater–streamwater flow pathway showed the consistent increase in d between precipitation and soil water, followed by more stable d values in groundwater and streamwater (Figure 6).

DISCUSSION

Evaporation is likely a much smaller part of ET than transpiration based on previous work at HBEF

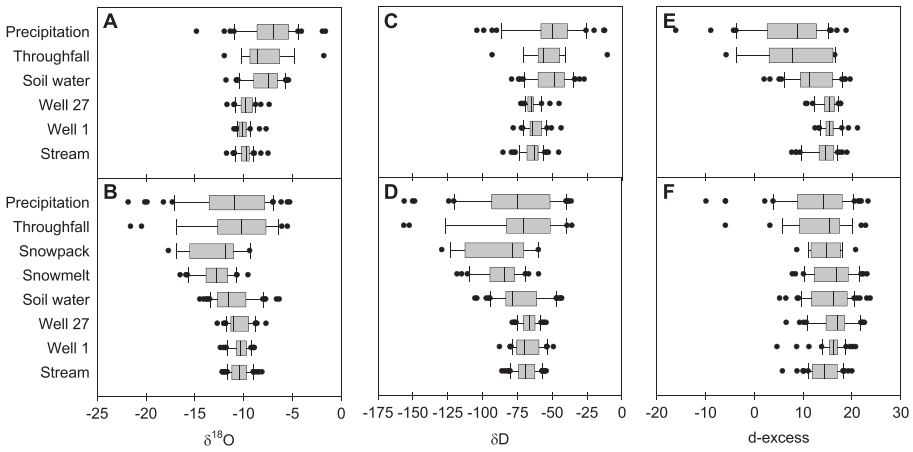

Figure 5. Box plots showing $\delta^{18}O$, δD, and *d* for different water sources during the growing (a, c, and e) and dormant (b, d, f) seasons

Table I. Comparison of water source *d* (‰) along the flow pathways using the Mann–Whitney rank sum test

Sources compared (A *vs* B)	Median *d* source A	Inter-quartile range source A	Median *d* source B	Inter-quartile range source B	Mann–Whitney *p*-value
Annual					
Precipitation vs streamflow	11.23	6.10–15.57	14.47	12.57–16.56	<0.001
Input vs soil water	12.26	7.54–16.87	14.50	10.76–17.78	0.023
Soil water vs well 1	14.50	10.76–17.78	16.03	14.53–17.73	0.023
Soil water vs well 27	14.50	10.76–17.78	15.79	15.09–16.93	0.039
Well 1 *versus* Well 27	16.03	14.53–17.73	15.79	15.09- 16.93	0.913
Well 1 *versus* streamflow	16.03	14.53–17.73	15.84	13.82–16.82	0.222
Well 27 *versus* streamflow	15.79	15.09- 16.93	15.84	13.82–16.82	0.229
Dormant season					
Precipitation *versus* snowpack	13.67	10.00–16.16	14.68	11.65–17.56	0.167
Throughfall *versus* snowmelt	15.35	10.34–17.23	16.71	11.80–16.96	0.354
Precipitation *versus* snowmelt	13.67	10.00–16.16	16.71	11.80–16.96	0.057
Precipitation *versus* throughfall	14.06	9.81–16.30	15.35	9.62–17.32	0.587
Throughfall *versus* snowpack	15.27	9.98–17.27	14.68	11.65–17.56	0.544
Snowpack *versus* snowmelt	14.68	11.65–17.56	16.71	11.80–16.96	0.949
Input *versus* soil water	16.30	11.19–18.37	16.29	11.79–18.98	0.521
Growing season					
Precipitation *versus* throughfall	3.29	–0.942–13.53	7.83	3.17–15.87	0.125
Throughfall *versus* soil water	7.83	3.17–15.87	10.26	7.56–14.24	0.491
Input *versus* soil water	8.96	2.69–12.60	11.20	9.47–15.92	<0.001

(e.g. Federer and Lash, 1978) and recent global results (Jasechko *et al.*, 2013). However, we expected to find isotopic evidence of evaporation from the catchment, especially during the growing season. This would be consistent with previous isotope studies in forested catchments (Tsujimura and Tanaka, 1998; Kubota and Tsuboyama, 2004) and with an estimated 37% of annual precipitation that is lost as evaporation plus transpiration at HBEF based on water balance (Campbell *et al.*, 2010). Increasing *d* values along hydrologic pathways are rarely reported in the literature; past studies where this has been observed are in continental systems with high evaporation and re-condensation (water recycling) rates (Gat and Matsui, 1991; Machavaram and Krishnamurthy, 1995). We are showing a similar pattern at a much smaller scale. Trends of *d* values along flow pathways in near-surface and sub-surface waters are not well established. By comparing the *d* values of source waters, we identified where *d* increases in the system: the growing season shallow and deep soils, and perhaps incrementally between the dormant season canopy and snowpack. The lack of isotopic evidence for evaporation and strong evidence for net condensation was surprising.

Explaining the pattern of increased *d* in soil water requires understanding soil water sources as sampled by the lysimeter. We assume that shallow soil water (top 10 cm) after a precipitation event was precipitation, and thus, the isotopic composition would be the same, because there was not a significant difference between

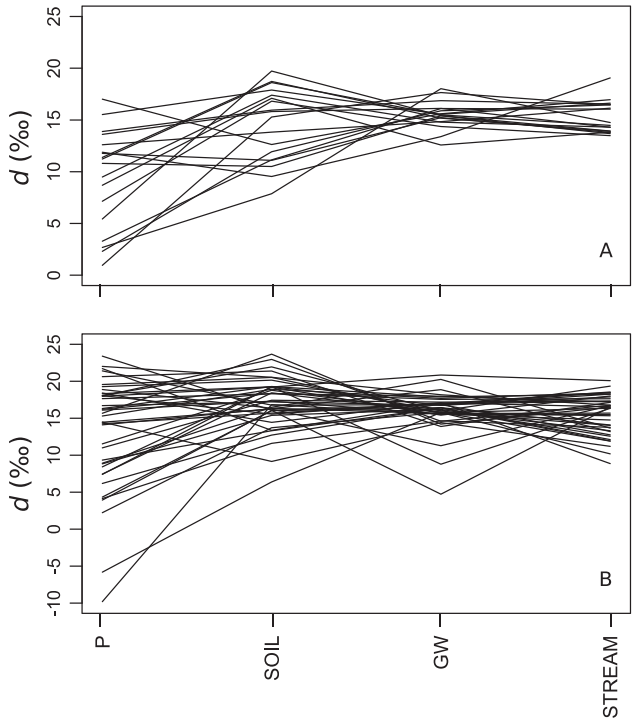

Figure 6. Lines show the different *d* of water along the major hydrologic flow pathway (precipitation-to-soil-to-groundwater-to-streamwater) on dates when all sources were present. Panel A shows the growing season, and panel B shows the dormant season

precipitation and throughfall (Table I). Between precipitation events, soil water that did not drain from the lysimeter would be subject to evaporation and transpiration losses – there were plants and seedlings growing in the lysimeter soil – and water vapour inputs. The sources of water vapour for water vapour inputs include evaporated soil and canopy water, transpired soil water, and advected vapour from the super-canopy environment (Figure 7). Thus, because we are working with three potential sources of water vapour to sub-canopy vapour, we cannot use a simple two-component mixing model (Froehlich *et al.*, 2008; Kong *et al.*, 2013) to quantify the sub-canopy recycling. Instead, we propose two scenarios that we hypothesize most likely cause the observed increase of growing season soil *d*.

The first scenario involves preferential loss of low *d* water from the soil by transpiration during the day and re-condensation of sub-canopy water vapour at night (right side of Figure 7). Transpired water would have the same *d* as the soil water (Dawson and Simonin, 2011), the kinetically evaporated water vapour would have a higher *d* than the soil water (Simonin *et al.*, 2014), and the advected super-canopy vapour would have an unknown *d* given our lack of measurement. Some of the transpired water would be transported from the sub-canopy environment; we assume that this fraction lost to the super-canopy is larger than the vapour evaporated from the soil because of the anticipated larger magnitude of transpiration relative to evaporation and the greater transport distance necessary for evaporated soil water. Thus, the evaporated and transpired water vapour retained in the sub-canopy environment would have a net increase in *d* because of the relatively larger loss of transpiration to the super-canopy environment. This scenario requires the assumption that mixing of advected

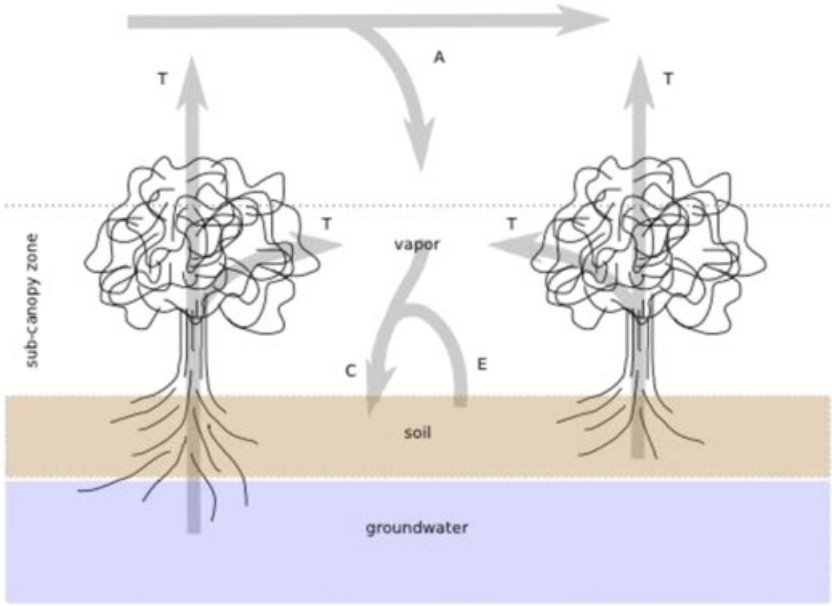

Figure 7. A conceptual model of how *d* could increase in the sub-canopy environment between rain events. The figure highlights the water budget for the sub-canopy zone, including relevant fluxes [i.e. transpiration (*T*), evaporation (*E*), condensation (*C*), and advected water vapour (*A*)] and stocks (i.e. sub-canopy water vapour, soil, and groundwater)

water vapour from the super-canopy environment would not be great enough to compensate for this net increase in sub-canopy water vapour d, which is the source for equilibrium condensation inputs.

One notable study lays out a similar argument to our first scenario. Liu *et al.* (2007) observed higher d in fog drip water compared with precipitation d in southwestern China. Their explanation for the higher d water vapour source involved greater evaporation during dry periods; however, soil water in their study did not retain this higher d from the fog drip. Thus, they did not propose a mechanism, as we have, by which low d water could be lost from the forest.

The second scenario is similar to the first scenario, except with higher d values for transpiration because of trees accessing groundwater (left side of Figure 7). Our first scenario assumed that soil water was the sole source to transpiration; however, some groundwater use by trees is expected given the evidence from previous studies (Dawson, 1996) and frequent water table incursion into the rooting zone at HBEF (Gannon *et al.*, 2014). The shallow groundwater carries a low $\delta^{18}O$ value throughout the growing season (Figure 4; median $\delta^{18}O$ of well 27 = −10.2), which is evidence of snowmelt as a source of recharge (Rodhe, 1998). Further, snowmelt carries a low median d value ($d = 16.7$), similar to well 27 during the growing season ($d = 15.7$). Episodic incursion of groundwater into the rooting zone mixes with soil water and may affect the composition of transpiration water source. If trees are influenced by groundwater, their transpiration values would be higher than if only shallow soil were the water source, and thus, the increased d in growing season soil water could be because of condensation of a water vapour source that is composed of both soil evaporation and transpiration of groundwater. Again in this scenario, the role of advected super-canopy vapour as a source is uncertain.

These two scenarios describe why sub-canopy water vapour d might be elevated relative to soil water during the growing season. However, the transport of this vapour to the soil and then to the lysimeter collector remains uncertain. Condensation is the most likely process for the transport of water vapour to soil water. At HBEF, evidence is lacking for dew formation on the ground surface and for canopy dew drip, and downwelling longwave radiation from the canopy typically prevents dew formation. Fog is also not commonly observed at HBEF. The transport of soil water to the lysimeter collector was assumed to follow simple displacement. The lysimeter tray held 10 cm of soil; thus, there was possibly 2.5 cm of water stored in that soil [assuming a field capacity of about 0.25 – based on unpublished data from Federer (personal communication)]. Any weekly precipitation less than 2.5 cm may be primarily displacement of soil water (Horton and Hawkins, 1965). Hydraulic lift from groundwater to soil water is unlikely in our lysimeters given the impermeable lysimeter floor. The continued increase in d between soil and groundwater (Table I) should be interpreted cautiously because the groundwater and streamwater samples have source areas from higher elevations where snow and condensation dynamics are different.

CONCLUSIONS

Testing our scenarios will require additional energy and water balance measurements, isotopic measurements, primarily measuring water vapour isotopic composition profiles from the within soil to the super-canopy environment at HBEF. Such measurements have successfully identified novel water vapour dynamics in the sub-canopy environment (Berkelhammer *et al.*, 2013; Zhao *et al.*, 2014). Direct measurement of soil water isotopic composition across soil depth profiles would also improve our understanding of where the high d water occurs, and such information combined with tree sap stable water isotopic composition would help identify sources of water for transpiration (Dawson, 1993, Brooks *et al.,* 2010, Evaristo *et al.*, 2015). Finally, more extensive measurement of throughfall isotopic composition would help interpret the sub-canopy d dynamics. Our measurements of throughfall suggested no changes in δD and $\delta^{18}O$ compared with precipitation, while the difference in d was less apparent [no significant increase (Table I); however, 69% of paired precipitation-throughfall samples showed a decrease in d].

Our results show a location where an increase in soil water d masked any evaporation signal in soil water isotopes, suggesting a microclimate that favours soil water recycling over soil evaporation at the HBEF. Examination of d in a broader set of global catchments may show the extent of increased d in soil water. For example, Geris *et al.* (2015) show soil water stable isotope values that plot above the LMWL during pre-event conditions at a Scottish catchment, consistent with our observations.

We do not expect that soil water recycling plays an important role in the volume of water entering HBEF soils but rather provides a consistent, small input that could stimulate soil heterotrophic organisms and their role in ecosystem processes (e.g. Biederbeck *et al.*, 1977). The sub-canopy meteorology required to produce strong soil water recycling, as we suggest, may have broader ecological implications, particularly related to processes dependent on temperature and humidity. Future work is needed to determine the extent of sub-canopy water vapour transport and its ecological importance.

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REFERENCES

Asano Y, Compton JE, Church MR. 2006. Hydrologic flowpaths influence inorganic and organic nutrient leaching in a forest soil. *Biogeochemistry* **81**: 191–204.

Bailey AS, Hornbeck JW, Campbell JL, Eagar C. 2003. Hydrometeorological database for Hubbard Brook Experimental Forest: 1955–2000. U.S. Forest Service, General Technical Report 305.

Bailey SW, Brousseau PA, McGuire KJ, Ross DS. 2014. Influence of landscape position and transient water table on soil development and carbon distribution in a steep, headwater catchment. *Geoderma* **226–227**: 279–289.

Barth JAC, Freitag H, Fowler HJ, Smith A, Ingle C, Karim A. 2007. Water fluxes and their control on the terrestrial carbon balance: Results from a stable isotope study on the Clyde Watershed (Scotland). *Applied Geochemistry* **22**: 2684–2694.

Battles JJ, Fahey TJ, Driscoll CT, Blum JD, Johnson CE. 2013. Restoring soil calcium reverses forest decline. *Environmental Science & Technology Letters* **1**(1): 15–19.

Benettin P, Bailey SW, Campbell JL, Green MB, Rinaldo A, McGuire KJ, Botter G. 2015. Modeling travel time distributions to estimate stream solute dynamics at the Hubbard Brook Experimental Forest, NH, USA. *Water Resources Research* DOI:10.1002/2015WR017552.

Berkelhammer M, Hu J, Bailey A, Noone DC, Still CJ, Barnard H, Gochis D, Hsiao GS, Rahn T, Turnipseed A. 2013. The nocturnal water cycle in an open-canopy forest. *Journal of Geophysical Research, [Atmospheres]* **118**: 10,225–10,242.

Biederbeck VO, Campbell CA, Nicholaichuk W. 1977. Simulated dew formation and microbial growth in soil of a semiarid region of western Canada. *Canadian Journal of Soil Science* **57**: 93–102.

Brooks JR, Barnard HR, Coulombe R, McDonnell JJ. 2010. Ecohydrologic separation of water between trees and streams in a Mediterranean climate. *Nature Geoscience* **3**: 100–104.

Campbell JL, Mitchell MJ, Mayer B, Groffman P, Christenson L. 2007. Mobility of nitrogen-15-labeled nitrate and sulfur-34-labeled sulfate during snowmelt. *Soil Science Society of America Journal* **71**: 1934–1944.

Campbell JL, Ollinger SV, Flerchinger GN, Wicklein H, Hayhoe K, Bailey AS. 2010. Past and projected future changes in snowpack and soil frost at the Hubbard Brook experimental forest, New Hampshire, USA. *Hydrological Processes* **24**: 2465–2480.

Clark ID, Fritz P. 1997. *Environmental Isotopes in Hydrogeology*. Lewis Publishers: Boca Raton and New York.

Coleman ML, Shepherd TJ, Durham JJ, Rouse JE, Moore GR. 1982. Reduction of water with zinc for hydrogen isotope analysis. *Analytical Chemistry (Washington* **54**: 993–995.

Craig H. 1961. Isotopic variations in meteoric waters. *Science* **133**: 1702–1703.

Cui J, An S, Wang Z, Fang C, Liu Y, Yang H, Xu Z, Liu S. 2009. Using deuterium excess to determine the sources of high-altitude precipitation: implications in hydrological relations between sub-alpine forests and alpine meadows. *Journal of Hydrology* **373**: 24–33.

Dansgaard W. 1964. Stable isotopes in precipitation. *Tellus* **16**: 436–468.

Dawson TE. 1993. Hydraulic lift and water use by plants: implications for water balance, performance and plant-plant interactions. *Oecologia* **95**: 565–574.

Dawson TE. 1996. Determining water use by trees and forests from isotopic, energy balance and transpiration analyses: the roles of tree size and hydraulic lift. *Tree Physiology* **16**: 263–272.

Dawson TE, Simonin KA. 2011. The roles of stable isotopes in forest hydrology and biogeochemistry. In *Forest Hydrology and Biogeochemistry*, Levia DF, Carlyle-Moses D, Tanaka T (eds). Springer: Netherlands; 137–161.

Detty JM, McGuire KJ. 2010a. Topographic controls on shallow groundwater dynamics: implications of hydrologic connectivity between hillslopes and riparian zones in a till mantled catchment. *Hydrological Processes* **24**: 2222–2236.

Detty JM, McGuire KJ. 2010b. Threshold changes in storm runoff generation at a till-mantled headwater catchment. *Water Resources Research* **46**: W07525. DOI:10.1029/2009WR008102.

DeWalle DR, Edwards PJ, Swistock BR, Aravena R, Drimmie RJ. 1997. Seasonal isotope hydrology of three Appalachian forest catchments. *Hydrological Processes* **11**: 1895–1906.

Evaristo J, Jasechko S, McDonnell JJ. 2015. Global separation of plant transpiration from groundwater and streamflow. *Nature* **525**(7567): 91–94.

Fahey TJ, Siccama TG, Driscoll CT, Likens GE, Campbell J, Johnson CE, Battles J, Aber JD, Cole JJ, Fisk MC, Groffman PM, Hamburg SP, Holmes RT, Schwarz PA, Yanai RD. 2005. The biogeochemistry of carbon at Hubbard Brook. *Biogeochemistry* **75**: 109–179.

Federer CA, Lash D. 1978. Simulated streamflow response to possible differences in transpiration among species of hardwood trees. *Water Resources Research* **14**: 1089–1097.

Ferretti DF, Pendall E, Morgan JA, Nelson JA, LeCain D, Mosier AR. 2003. Partitioning evapotranspiration fluxes from a Colorado grassland using stable isotopes: Seasonal variations and ecosystem implications of elevated atmospheric CO2. *Plant and Soil* **254**: 291–303.

Froehlich K, Kralik M, Papesch W, Rank D, Scheifinger H, Stichler W. 2008. Deuterium excess in precipitation of alpine regions - moisture recycling. *Isotopes in Environmental and Health Studies* **44**: 61–70.

Gannon JP, Bailey SW, McGuire KJ. 2014. Organizing groundwater regimes and response thresholds by soils: a framework for understanding runoff generation in a headwater catchment. *Water Resources Research* **50**: 8403–8419.

Gat JR. 1996. Oxygen and hydrogen isotopes in the hydrologic cycle. *Annual Review of Earth and Planetary Sciences* **24**: 225–262.

Gat JR, Matsui E. 1991. Atmospheric water balance in the Amazon basin: an isotopic evapotranspiration model. *Journal of Geophysical Research* **96**: 13179–13188.

Geris J, Tetzlaff D, Soulsby C. 2015. Resistance and resilience to droughts: hydropedological controls on catchment storage and run-off response. *Hydrological Processes* **29**(21): 4579–4593.

Gibson JJ, Edwards TWD. 2002. Regional water balance trends and evaporation–transpiration partitioning from a stable isotope survey of lakes in northern Canada. *Global Biogeochemical Cycles* **16**: 10–11.

Gonfiantini R. 1986. Environmental isotopes in lake studies. In *Handbook of environmental isotope geochemistry*, Fritz P, Fontes J (eds). Elsevier: New York; 113–168.

Hill AR. 1993. Nitrogen dynamics of storm runoff in the riparian zone of a forested watershed. *Biogeochemistry* **20**: 19–44. DOI:10.1002/hyp.6004.

Hooper RP, Shoemaker CA. 1986. A comparison of chemical and isotopic hydrograph separation. *Water Resources Research* **22**: 1444–1454.

Hornbeck JW, Martin CW, Eagar C. 1997. Summary of water yield experiments at Hubbard Brook experimental forest, New Hampshire. *Canadian Journal of Forest Research* **27**: 2043–2052.

Horton JH, Hawkins RH. 1965. Flow path of rain from the soil surface to the water table. *Soil Science* **100**: 377–383.

Jasechko S, Sharp ZD, Gibson JJ, Birks SJ, Yi Y, Fawcett PJ. 2013. Terrestrial water fluxes dominated by transpiration. *Nature* **496**: 347–350.

Kabeya N, Katsuyama M, Kawasaki M, Ohte N, Sugimoto A. 2007. Estimation of mean residence times of subsurface waters using seasonal variation in deuterium excess in a small headwater catchment in Japan. *Hydrological Processes* **21**: 308–322.

Kirchner JW, Tetzlaff D, Soulsby C. 2010. Comparing chloride and water isotopes as hydrological tracers in two Scottish catchments. *Hydrological Processes* **24**: 1631–1645.

Kong Y, Pang Z, Froehlich K. 2013. Quantifying recycled moisture fraction in precipitation of an arid region using deuterium excess. *Tellus B* **65**: 19251. DOI:10.3402/tellusb.v65i0.19251.

Kubota T, Tsuboyama Y. 2004. Estimation of evaporation rate from the forest floor using oxygen-18 and deuterium compositions of throughfall and stream water during a non-storm runoff period. *Journal of Forest Research* **9**: 51–59.

Lachniet MS, Patterson WP. 2002. Stable isotope values of Costa Rican surface waters. *Journal of Hydrology* **260**: 135–150.

Lai C-T, Ehleringer JR. 2010. Deuterium excess reveals diurnal sources of water vapor in forest air. *Oecologia* **165**: 213–223.

Laudon H, Hemond HF, Krouse R, Bishop KH. 2002. Oxygen 18 fractionation during snowmelt: implications for spring flood hydrograph separation. *Water Resources Research* **38**: 1258.

Lee KS, Kim JM, Lee DR, Kim Y, Lee D. 2007. Analysis of water movement through an unsaturated soil zone in Jeju Island, Korea using stable oxygen and hydrogen isotopes. *Journal of Hydrology* **345**: 199–211.

Leonard RE. 1961. Net precipitation in a northern hardwood forest. *Journal of Geophysical Research* **66**: 2417–2421.

Likens GE. 2013. *Biogeochemistry of a Forested Ecosystem*, 3rd edition. Springer: New York.

Lis G, Wassenaar LI, Hendry MJ. 2008. High-precision laser spectroscopy D/H and 18O/16O measurements of microliter natural water samples. *Analytical Chemistry* **80**: 287–293.

Liu WJ, Liu WY, Li PJ, Gao L, Shen YX, Wang PY, Zhang YP, Li HM. 2007. Using stable isotopes to determine sources of fog drip in a tropical seasonal rain forest of Xishuangbanna, SW China. *Agricultural and Forest Meteorology* **143**(1): 80–91.

Lovett GM, Nolan SS, Driscoll CT, Fahey TJ. 1996. Factors regulating throughfall flux in a New Hampshire forest landscape. *Canadian Journal of Forest Research* **26**: 2134–2144.

Machavaram MV, Krishnamurthy RV. 1995. earth surface evaporative process: a case study from the great lakes region of the United States based on deuterium excess in precipitation. *Geochimica et Cosmochimica Acta* **59**: 4279–4283.

McGlynn BL, McDonnell JJ, Shanley JB, Kendall C. 1999. Riparian zone flowpath dynamics during snowmelt in a small headwater catchment. *Journal of Hydrology* **222**: 75–92.

McGuire KJ, DeWalle DR, Gburek WJ. 2002. Evaluation of mean residence time in subsurface waters using oxygen-18 fluctuations during drought conditions in the mid-Appalachians. *Journal of Hydrology* **261**: 132–149.

McGuire KJ, McDonnell JJ. 2006. A review and evaluation of catchment transit time modeling. *Journal of Hydrology* **330**: 543–563.

Moreira M, Sternberg L, Martinelli L, Victoria R, Barbosa E, Bonates L, Nepstad D. 1997. Contribution of transpiration to forest ambient vapour based on isotopic measurements. *Global Change Biology* **3**: 439–450.

Rhoads AG, Hamburg SP, Fahey TJ, Siccama TG, Hane EN, Battles JJ, Cogbill C, Randall J, Wilson G. 2002. Effects of an intense ice storm on the structure of a northern hardwood forest. *Canadian Journal of Forest Research* **32**(10): 1763–1775.

Richardson AD, Bailey AS, Denny EG, Martin CW, O'Keefe J. 2006. Phenology of a northern hardwood forest canopy. *Global Change Biology* **12**: 1174–1188.

Rodhe A. 1998. Snowmelt-dominated systems. In *Isotope Tracers in Catchment Hydrology*, Kendall C, McDonnell JJ (eds). Elsevier: Amsterdam; 391–433.

Rothfuss Y, Biron P, Braud I, Canale L, Durand JL, Gaudet JP, Richard P, Vauclin M, Bariac T. 2010. Partitioning evapotranspiration fluxes into soil evaporation and plant transpiration using water stable isotopes under controlled conditions. *Hydrological Processes* **24**: 3177–3194.

Scanlon BR, Healy RW, Cook PG. 2002. Choosing appropriate techniques for quantifying groundwater recharge. *Hydrogeology Journal* **10**: 18–39.

Shanley JB, Kendall C, Smith TE, Wolock DM, McDonnell JJ. 2002. Controls on old and new water contributions to stream flow at some nested catchments in Vermont, USA. *Hydrological Processes* **16**: 589–609.

Simonin KA, Link P, Rempe D, Miller S, Oshun J, Bode C, Dietrich WE, Fung I, Dawson TE. 2014. Vegetation induced changes in the stable isotope composition of near surface humidity. *Ecohydrology* **7**: 936–949.

Sklash MG, Farvolden RN. 1979. The role of groundwater in storm runoff. *Journal of Hydrology* **43**: 45–65.

St. Amour NA, Gibson JJ, Edwards TWD, Prowse TD, Pietroniro A. 2005. Isotopic time-series partitioning of streamflow components in wetland-dominated catchments, lower Liard River basin, Northwest Territories, Canada. *Hydrological Processes* **19**: 3357–3381.

Sutanto SJ, van den Hurk B, Dirmeyer PA, Seneviratne SI, Röckmann T, Trenberth KE, Blyth EM, Wenninger J, Hoffmann G. 2014. HESS opinions "A perspective on isotope versus non-isotope approaches to determine the contribution of transpiration to total evaporation.". *Hydrology and Earth System Sciences* **18**: 2815–2827.

Tsujimura M, Tanaka T. 1998. Evaluation of evaporation rate from forested soil surface using stable isotopic composition of soil water in a headwater basin. *Hydrological Processes* **12**: 2093–2103.

Twining J, Stone D, Tadros C, Henderson-Sellers A, Williams A. 2006. Moisture Isotopes in the Biosphere and Atmosphere (MIBA) in Australia: a priori estimates and preliminary observations of stable water isotopes in soil, plant and vapour for the Tumbarumba Field Campaign. *Global and Planetary Change* **51**: 59–72.

Wang XF, Yakir D. 2000. Using stable isotopes of water in evapotranspiration studies. *Hydrological Processes* **14**: 1407–1421.

Welp LR, Lee X, Griffis TJ, Wen X-F, Xiao W, Li S, Sun X, Hu Z, Val Martin M, Huang J. 2012. A meta-analysis of water vapor deuterium-excess in the midlatitude atmospheric surface layer. *Global Biogeochemical Cycles* **26**: GB3021.

Zhao L, Wang L, Liu X, Xiao H, Ruan Y, Zhou M. 2014. The patterns and implications of diurnal variations in the d-excess of plant water, shallow soil water and air moisture. *Hydrology and Earth System Sciences* **18**: 4129–4151.

Zhang W, Cheng B, Hu Z, An S, Xu Z, Zhao Y, Xu Q. 2010. Using stable isotopes to determine the water sources in alpine ecosystems on the east Qinghai-Tibet Plateau, China. *Hydrological Processes* **24**: 3270–3280.

