@AGU_PUBLICATIONS



Geophysical Research Letters

RESEARCH LETTER

10.1002/2015GL064622

Key Points:

- TTDs are affected by throughfall isotope data
- A simple correction factor can partly account for throughfall effects
- Using throughfall isotope data is necessary for accurate TTD estimates

Supporting Information:

Texts S1 and S2 and Figures S1–S9

Correspondence to: M. P. Stockinger, m.stockinger@fz-juelich.de

Citation:

Stockinger, M. P., A. Lücke, J. J. McDonnell, B. Diekkrüger, H. Vereecken, and H. R. Bogena (2015), Interception effects on stable isotope driven streamwater transit time estimates, *Geophys. Res. Lett.*, *42*, 5299–5308, doi:10.1002/ 2015GL064622.

Received 20 MAY 2015 Accepted 11 JUN 2015 Accepted article online 16 JUN 2015 Published online 8 JUL 2015

Interception effects on stable isotope driven streamwater transit time estimates

Michael P. Stockinger¹, Andreas Lücke¹, Jeffrey J. McDonnell^{2,3}, Bernd Diekkrüger⁴, Harry Vereecken¹, and Heye R. Bogena¹

¹Institute of Bio- and Geosciences, Agrosphere Institute, Forschungszentrum Jülich GmbH, Jülich, Germany, ²Global Institute for Water Security, University of Saskatchewan, Saskatoon, Saskatchewan, Canada, ³School of Geosciences, University of Aberdeen, Aberdeen, UK, ⁴Department of Geography, Bonn University, Bonn, Germany

Abstract Previous studies of streamwater transit time distributions (TTDs) used isotope tracer information from open precipitation (OP) as inputs to lumped watershed models that simulate the stream isotopic composition to estimate TTD. However, in forested catchments passage of rainfall through the canopy will alter the tracer signature of throughfall (TF) via interception. Here we test the effect of using TF instead of OP on TTD estimates. We sampled a 0.39 km² catchment (Wüstebach, Germany) for a 19 month period using weekly precipitation and stream isotope data to evaluate changes in stream isotope simulation and TTDs. We found that TF had different effects on TTDs for δ^{18} O and δ^{2} H, with TF leading to up to 4 months shorter transit times. TTDs converged for both isotopes only when using TF. TF improved the stream isotope simulations. These results demonstrate the importance of canopy-induced isotope tracer changes in estimating streamwater TTDs in forested catchments.

1. Introduction

The stable isotopes of water (δ^2 H and δ^{18} O) are conservative tracers of water movement. Many studies have used them for estimating the mean transit time (MTT) of precipitation through a catchment and the respective streamwater transit time distribution (TTD) [*McGuire and McDonnell*, 2006]. Recently, much work focused on the relation between the TTD and catchment characteristics [*Hrachowitz et al.*, 2009; *Tetzlaff et al.*, 2009], on the time-varying nature of transit times [*Heidbüchel et al.*, 2012; *Rinaldo et al.*, 2011], on incomplete mixing of tracer signals in the soil [*Brooks et al.*, 2010], and on differences in transit times of precipitation, resident soil water, groundwater, and streamwater [*Botter et al.*, 2011; *Hrachowitz et al.*, 2013a].

Most studies of TTD to date have assumed that precipitation δ^2 H and δ^{18} O are unaffected by passage through the vegetation canopy to the soil surface. However, forest canopies affect precipitation by interception, reducing the total volume of precipitation by evaporation, thus generating throughfall (TF). Interception, canopy evaporation, and drip occur mainly on leaves and can change the stable isotope tracer signal of water reaching the forest floor via isotopic fractionation [*Cappa et al.*, 2003]. The infiltrating TF can therefore be isotopically enriched compared to open precipitation (OP) [*Dewalle and Swistock*, 1994].

Previous studies that have investigated the differences between TF isotope composition (δ TF) and OP isotope composition (δ OP) have focused on (a) isotopic enrichment during canopy evaporation and subsequent canopy drip [*Saxena*, 1986]; (b) complete evaporation of residual interception water after the secession of rainfall, taking into account the temporally nonuniform isotope signal of single precipitation events [*Berman et al.*, 2009; *Celle-Jeanton et al.*, 2004; *Saxena*, 1986]; (c) isotopic exchange with ambient air vapor [*Brodersen et al.*, 2000]; (d) rainfall partitioning processes within the canopy [*Kato et al.*, 2013]; and (e) mixing with residual canopy water of a prior rainfall event [*Allen et al.*, 2014].

In a hydrograph separation study *Kubota and Tsuboyama* [2003] measured δ TF and found a difference of up to 10% in the estimation of "old water" in runoff when compared to δ OP. *Asano et al.* [2002] used δ TF for the study of MTT in a forested catchment in Japan. However, no studies have yet compared the streamwater TTD model estimates when using δ TF instead of δ OP as tracer input.

Here we investigate the differences in streamwater TTD estimates emerging with δTF versus δOP as input to the TTD model. We focus on the well-studied forested Wüstebach catchment, Germany. Specifically, we address the following research questions: (1) How and to what extent are TTDs altered by using δTF

©2015. American Geophysical Union. All Rights Reserved.

Geophysical Research Letters



Figure 1. The Wüstebach test site (38.5 ha) with soil types and contour lines. Also shown are the subcatchment area of location 1 (violet, thick outline), the deforestation area (red outline), the groundwater reservoir and transport pipeline and the location of the TF and on-site OP samplers. Inset displays relative location of the test site to the climate stations Kalterherberg and Schöneseiffen.

instead of δOP ? (2) How does spruce forest canopy influence precipitation water volume and isotope composition of water that makes its way to the forest floor? (3) Is a simple correction factor for δOP able to adequately represent canopy influence in a TTD model?

2. Methods

2.1. Study Site

The Wüstebach headwater catchment (38.5 ha) is located in Germany (50°30'16"N, 6°20'00"E, WGS84) at 595 to 628 m above sea level (asl). The climate is humid temperate with mean annual precipitation of 1107 mm (1961–1990) and a mean annual temperature of 7°C [*Zacharias et al.*, 2011]. The Wüstebach test site is part of the Lower Rhine/Eifel Observatory of the Terrestrial Environmental Observatories (TERENO) network. The catchment is located in the Eifel national park and was homogeneously afforested after World War II with Norway spruce (*Picea abies*) and Sitka spruce (*Picea sitchensis*) [*Etmann*, 2009]. The bedrock consists of Devonian shale with sporadic inclusions of sandstone [*Richter*, 2008]. Soils are up to 2 m deep with an average depth of 1.6 m [*Graf et al.*, 2014]. Food and Agriculture Organization soil types of cambisol and planosol/cambisol are found on hillslopes, while gleysols, histosols, and planosols are found in the riparian zone. The catchment had a manmade structure (since World War II) that consisted of a pipe that routed groundwater from a groundwater spring located in the catchment directly downstream to the stream, enabling a portion of catchment groundwater to bypass the soil matrix. This pipe was shut down in Spring 2011. In September 2013, 9 ha were clear-cut as part of the national park development [*Bogena et al.*, 2014] (Figure 1).

2.2. Measured Data

We used hydrological measurements and isotope data from 3 October 2012 to 21 April 2014. TF was measured with six TF samplers (RS200, UMS GmbH, Germany). The TF sampling approach followed *World Meteorological Organization* [2008] specifications. Each sampler consisted of a 50 cm pipe (diameter: 20 cm) buried in the forest soil (30 cm), and a 100 cm pipe with a collection funnel (area: 314 cm^2) inserted on top (Figure S1 in the supporting information). To protect against litterfall, a metal mesh with 5 mm diameter holes was placed in the funnel. TF was led via a plastic hose (inner diameter: 4 mm) to a sample bottle inside the buried pipe to prevent evaporation losses. The funnel outlet was covered by a table tennis ball as an additional barrier against evaporation. The samplers were placed 2 m from tree trunks at a 2 m spacing (Figure S1). The spatial representativeness of the sampled TF volumes was tested by comparing them to TF volumes of a second TF sampling system operated by the University of Trier in a distance of 50 m. However, due to a lack of protective measures against evaporation, this system was inappropriate for isotope sampling and thus no further data of it was used in this study (Figure S2).

In May 2013, two OP samplers were installed in a small clearing in the Wüstebach catchment, measuring OP on-site for 11 months. Due to the shortness of this time series, we did not use them for TTD estimation but only for the calculation of interception loss (difference of OP to TF) and the differences between δ TF and δ OP.

OP volume used as model input was acquired at 1 h intervals in 0.1 mm increments from the Kalterherberg meteorological station (German Weather Service, station number 80,115, 535 m asl) located 9 km northwest of Wüstebach. The Kalterherberg data were validated for Wüstebach by regression to the on-site OP measurements of the clearing and to precipitation data from a rain gauge (Pluvio², Ott, Kempten, Germany) installed in the clear-cut area of Wüstebach (available from January 2014 onward). Model input δ OP was acquired from a site 3 km to the NE at the Schöneseiffen meteorological station (620 m asl). This site has a time series of weekly isotope samples available from 2009 to the present.

δTF and δOP (onsite, Figure 1) were collected in weekly intervals. Due to organizational and technical issues, deviations from routine sampling occurred leading to the shortest and the longest intervals being 4 and 35 days, respectively. We measured water volumes of all TF and OP samplers (six under canopy, two in clearing) in 10 ml increments (50 ml increments from 18 December 2012 to 1 August 2013) and took samples for isotope analyses in 50 ml HDPE bottles. Field experiments with the TF samplers using water of known isotopic value showed no significant evaporative enrichment of isotope values over a 21 day period (see supporting information for details). To calculate precipitation volume (mm) we used the arithmetic mean of all TF and OP samplers, while the volume-weighed mean was calculated for isotope values. During four sampling weeks, needle litter blocked the TF system, which led to standing water pools in the funnels. Consequently, these weeks were not considered in the further analyses.

Water isotopic analysis was carried out using an Isotope-Ratio Mass Spectrometer (IRMS, Delta V Advantage, Thermo Scientific) coupled with a high-temperature pyrolysis furnace (HT-O, HEKAtech). Results are reported as δ values relative to Vienna Standard Mean Ocean Water (VSMOW) [*Gonfiantini*, 1978]. Internal standards calibrated against VSMOW, Standard Light Antarctic Precipitation, and Greenland Ice Sheet Precipitation were used to ensure long-term stability of analyses. The precision of the analytical system was $\leq 0.1\%$ for δ^{18} O and $\leq 1.0\%$ for δ^{2} H.

2.3. TTD Calculation

We used the conceptual model TRANSEP [*Weiler et al.*, 2003] for TTD estimation. TRANSEP uses the convolution integral to calibrate effective precipitation p_{eff} by simulating the outlet's hydrograph:

$$Q(t) = \int_0^t g(\tau_R) p_{\text{eff}}(t - \tau_R) \mathrm{d}\tau_R \tag{1}$$

where Q(t) is the simulated runoff, $g(\tau_R)$ is the Response Time Distribution (RTD), τ_R is the response time, and $p_{eff}(t - \tau_R)$ the effective precipitation for time step $t - \tau_R$. According to catchment-wide wetness conditions the hydrograph was split into three modeling periods (Winter 2012, Summer 2013, and Winter 2013). The winter periods represent the catchment's wet state, whereas the summer period represents the dry state. Calculation of p_{eff} during dry state was based on a reduced runoff-generating area, representing hydrological disconnection of the Wüstebach's hillslopes from the runoff generation process (for more details, see *Stockinger et al.* [2014]). Using p_{eff} and a 2 year spin-up with mean values of all model input variables, TTDs were inferred by simulation of observed streamwater isotope composition using the convolution integral:

$$C(t) = \frac{\int_0^t C_{\rm in}(t - \tau_T) p_{\rm eff}(t - \tau_T) h(\tau_T) d\tau_T}{\int_0^t p_{\rm eff}(t - \tau_T) h(\tau_T) d\tau_T}$$
(2)

where C(t) is the stream water isotope concentration at time t, $C_{in}(t - \tau_T)$ is the precipitation isotope concentration at time t with travel time τ_T and $h(\tau_T)$ is the TTD.

RTD and TTD were estimated using the Two Parallel Linear Reservoir method, as it produced good results of TTD estimates for the Wüstebach (*Stockinger et al.* [2014]):

$$g(\tau_R) = \frac{\phi}{\tau_f} \exp\left(-\frac{\tau_R}{\tau_f}\right) + \frac{1-\phi}{\tau_s} \exp\left(-\frac{\tau_R}{\tau_s}\right)$$
(3)

$$h(\tau_T) = \frac{\phi}{\tau_f} \exp\left(-\frac{\tau_T}{\tau_f}\right) + \frac{1-\phi}{\tau_s} \exp\left(-\frac{\tau_T}{\tau_s}\right)$$
(4)

where ϕ is a partitioning factor (between 0 and 1) and τ_f and τ_s are the mean transit times of the fast and slow reservoir, respectively.

We used the Volumetric Efficiency ranging from 0 to 1 (1 indicating a perfect fit) as an objective function for hydrograph simulation, as it equally weighs the simulation quality of base flow and storm event conditions. In addition, the Nash-Sutcliffe Efficiency (NSE) was used to ensure that temporal stream isotope dynamics are adequately captured [*Criss and Winston*, 2008; *Nash and Sutcliffe*, 1970]:

$$VE = 1 - \frac{\sum |Q_{sim} - Q_{obs}|}{\sum Q_{obs}}$$
(5)

$$NSE = 1 - \frac{\sum (C_{obs} - C_{sim})^2}{\sum (C_{obs} - \overline{C_{obs}})^2}$$
(6)

The parameter space was searched using the Ant-Colony Optimization (ACO) algorithm [*Abbaspour et al.*, 2001]. Parameter uncertainties for stream isotope simulation results and TTD estimates were obtained by using the 95% confidence limits of the posterior parameter distribution based on the last third of parameter sets used by ACO. The obtained 95% confidence limits were then used as parameter boundaries for 1000 Monte Carlo (MC) simulations (MATLAB toolbox "MCAT v.3), and we plot the minimum and maximum stream isotope and TTD values found by all 1000 MC runs. The given stream isotope uncertainties are the measurement precision of the IRMS.

As the outlet (location 14, Figure 1) showed an attenuated isotope signal, we additionally simulated C(t) of the isotopically more dynamic spring (location 1) to further explore differences in simulation results when using δOP or δTF . To do this, we used the outlet-calibrated p_{eff} with stream isotope data of the spring with equation (2). TTDs were compared by evaluating the absolute and relative changes in transit time at 10, 25, 50, 75, and 90 quantiles, respectively, as well as identifying the maximum change in TTD. This was done to compare the behavior of both TTD curves for shorter and longer transit times.

To test if missing δ TF data in TTD estimation can be approximated with an ordinary δ OP correction approach, we used a general factor of 0.5‰ added to the measured δ^{18} O values of δ OP as a means to account for canopy influence (δ OP_{corr}). This factor was already used for isotope modeling of the Wüstebach catchment by *Stockinger et al.* [2014] for a period where no δ TF data were available. Its value was found empirically through inverse modeling, and it produced a better fit of observed stream isotope values than δ OP.

3. Results and Discussion

Comparison of OP volume from the Kalterherberg rain gauge with the two on-site measured precipitation time series showed strong agreement ($R^2 = 0.96$ with 95% significance $p = 1.8 \times 10^{-9}$ and $R^2 = 0.92$ with $p = 4.3 \times 10^{-21}$). Both regressions were close to the 1:1 line (slopes = 0.95 and 1.06), indicating that the Kalterherberg station represents reliable OP input data for hydrological modeling of the Wüstebach. This was further supported by the almost complete closure (>97%) of the Wüstebach catchment water balance for a period of 3 years when using Kalterherberg station data [*Graf et al.*, 2014].

3.1. Interception Effects on Throughfall

The time series of model input δ OP and δ TF showed a typical seasonal isotope signal (Figure S5), with measured δ^{18} O variations ranging from -16.40 to -2.77% in δ OP and from -14.27 to -3.04% in δ TF. The absolute difference between δ OP and δ TF ranged between -0.98 and +1.29% δ^{18} O and -8.20 and +11.50% δ^{2} H. These differences are comparable to those found in a similar study by *Dewalle and Swistock* [1994].

TF volume increased with increasing OP volume with a slope of 0.77 and $R^2 = 0.92$ (n = 35, Figure S6). *Peng et al.* [2014] found similar results in a Qinghai spruce forest and argued that the deviation from a slope of 1 was indicative of evaporative influence in the canopy. During the observation period, the measured average interception loss due to canopy evaporation was 41% with a standard deviation of 19%. This is consistent with *Brodersen et al.* [2000] who observed approximately 40% interception loss for a 130–170 year old spruce stand in the Black Forest, Germany. Similar to their study, no clear seasonal variations in interception loss or in isotopic changes between δ OP and δ TF were found in the present study. This can be explained by the different processes that induce isotopic changes (e.g., evaporation, mixing with residual canopy storage water) and by the weekly bulk samples, which aggregate different events.

3.2. How Did Throughfall Isotope Composition Affect Stream Isotope Simulation?

TRANSEP simulations using δ^{18} O of δ OP as input (results for δ^{2} H as well as details on hydrograph simulation are shown in the supporting information) were not able to adequately reproduce observed stream isotope values (Figures 2b and 2c) as indicated by low NSE values (0.44 for location 1 and 0.22 for location 14, respectively). When using δ OP_{corr}, NSE values increased to 0.67 (location 1) and 0.33 (location 14), and for δ TF simulations NSE values reached 0.61 (location 1) and 0.33 (location 14).

Generally, the obtained NSE values are similar to results of previous studies simulating δ^{18} O and δ^{2} H for stream [*Birkel et al.*, 2010, 2011] and soil water [*Windhorst et al.*, 2014]. While an NSE value of 0.33 is certainly low, it can be attributed to the emphasis of the NSE to time series peaks [*Criss and Winston*, 2008] and the attenuated tracer signal of location 14. For location 1 it can be observed that the second half of the time series was better modeled (NSE = 0.84) than the beginning (NSE = 0.05). The worse performance during the first half can be attributed to the incorrect input data of the spin-up, i.e., using mean values for all input variables. This also explains the almost nonexistent parameter uncertainty bands in the first half of the time series. The second half of the time series does not have this issue as can be seen in the drastically increased model performance and the widening of the parameter uncertainty bands.

The difference between δOP and δTF results is especially prominent for location 1 (Figure 2b). Here the simulation result of δOP mostly underestimated observed isotope values in the second half of the time series. In contrast, δTF results simulated this part considerably better. We attribute the deviation of δOP results from observed values to its inadequacy as an input variable for a forested catchment.

Comparing results for δOP_{corr} and δTF , we found most pronounced differences for the Summer 2013 seasonal isotope peak of location 1 (Figure 2b). Isotope simulation results based on δOP_{corr} showed higher isotope values in June 2013 as compared to results derived with δTF . δOP_{corr} overestimated observed values while δTF performed better (Figure 2b, green rectangle "June 2013"). Another example of the overall better performance of δTF is the August 2013 peak (Figure 2b, green rectangle "August 2013"). This peak was only reproduced by the isotope simulation using δTF but not using δOP_{corr} . In both cases, results based on δTF were closer to observed isotope values. However, the similar NSE values of both inputs indicate that δOP_{corr} can produce comparable stream isotope results.

Thus, regarding the stream isotope simulation, δOP_{corr} may serve as a plausible surrogate for missing δTF data. We note that the correction factor depends on site specifics such as climate conditions or vegetation type. For instance, *Calderon and Uhlenbrook* [2014] accounted for δTF enrichment in a tropical forest by adding 1.4‰ to isotope values, while *Stockinger et al.* [2014] applied a simple correction factor of adding 0.5‰ for the humid Wüstebach site.

Since no seasonal trend in isotopic changes was found for the Wüstebach catchment, a constant correction factor for δOP_{corr} seems appropriate. However, for locations showing strong seasonal trends, a time-varying

AGU Geophysical Research Letters



Figure 2. (a) Rainfall (blue bars from top) and observed runoff (black) together with simulated (red) runoff from hydrograph simulation in logarithmic scale for the three modeling periods. (b) and (c) Stream isotope simulation results for location 1 (spring) and location 14 (outlet) based on δ^{18} O. Observed stream isotopes with grey error bars compared to simulations using δ OP, δ OP_{corr}, and δ TF. Uncertainty boundaries are shown as dashed lines. Vertical, light grey dashed lines in all panels separate the three modeling periods, with thinner lines in Figure 2a delineating the deforestation period. Green rectangles in Figure 2b are discussed in the main text.

correction factor might be necessary. Further studies investigating the need for a time-varying correction factor are needed to address this issue.

3.3. How Did Throughfall Isotope Composition Affect Estimated TTD?

We found generally decreasing transit times for most quantiles when using δ TF instead of δ OP (Figure 3 and Table 1). These changes were much more pronounced for δ^2 H results, while δ^{18} O results showed only minor changes or no changes at all in the case of location 1. The maximum absolute difference in cumulative TTDs were observed when using δ^2 H with 7.5% occurring at 208 days transit time for location 1, while for location 14 it was 7.3% occurring at 145 days transit time (Figure 3c). The corresponding change in transit time



Figure 3. TTDs derived by using δ OP and δ TF and isotope tracer data of either δ^{18} O (O-OP and O-TF) or δ^{2} H (H-OP and H-TF) for (a) the spring (location 1) and (b) the outlet (location 14). Uncertainty boundaries are displayed as dashed lines. The violet line shows maximum change in transit time, and the insets highlight details of areas marked with red rectangles. (c) Absolute differences of cumulative TTDs (δ OP- δ TF) as a function of transit time.

was 119 days for location 1 and 85 days for location 14, respectively. Thus, for the Wüstebach, differences of approximately 2–4 months in transit times are possible. Similar results were found in a Cl^- tracer study of *Hrachowitz et al.* [2013a]. The differences in their study were caused by evaporative removal of young water from the interception storage leading to a change in tracer signal by evapoconcentration [*Harman*, 2015]. Given the overall differences between the obtained TTDs, the behavior of the catchment would be poorly characterized when using δ OP.

While δ^{18} O and δ^{2} H gave different results for δOP , the TTDs from both isotopes converge for δTF for both locations. For location 1, the uncertainty bounds of the δ TF-TTDs overlap with δOP -TTDs diverging from each other, while for location 14, δ TF-TTDs plot closer together than for δOP . Considering that isotopic fractionation during evaporation is more pronounced for $\delta^2 H$ than for δ^{18} O, we hypothesize that the lack of accounting for canopy evaporation could be the reason for the spread of δOP -TTDs. This effect would also explain differences in hydrograph separation observed by Lyon et al. [2009] for oxygen and hydrogen stable isotopes [Birkel et al., 2012]. Thus, when using incorrect input data for a forested catchment (δOP), the choice of isotopic tracer strongly influences TTD results. Only δTF converges to approximately the same solution.

We found variations in TTD quantiles ranging from 1 to 275 days transit time for both locations (Table 1 and Figures 3a, 3b, and S9 for δOP_{corr} -TTD). Using δOP_{corr} resulted in vastly different TTDs compared to δTF results. This affects the interpretation of, e.g., the relationships between catchment

characteristics and TTDs. Thus, contrary to stream isotope simulation, the applied simple TF correction factor is not sufficient for streamwater transit time estimates. Undoubtedly, measurement of δ TF is necessary to improve TTD estimates of forested catchments (e.g., for the TTD studies of *Timbe et al.* [2014] and *Heidbüchel et al.* [2012], conducted in forested or partly forested catchments).

The TTD is not directly measurable with current technologies. Thus, it is necessary to ensure that TTD estimates are as correct as possible. Our results show that the TTD is more reliable when using δTF instead of δOP . As the hydrological community currently faces the challenge of predicting the hydrology

	10%	25%	50%	75%	90%	
δ ¹⁸ 0						
			Location 1			
δΟΡ	14	40	106	280	761	
δOP _{corr}	13	37	94	209	486	
δTF	13	36	96	273	774	
			Location 14			
δΟΡ	31	98	336	755	1053	
δOP_{corr}	23	76	256	590	917	
δΤϜ	22	78	318	692	1001	
			Location 1			
$\Delta \delta OP_{corr}$	-1 (-7)	-3 (-8)	-12 (-11)	-71 (-25)	-275 (-36)	
$\Delta \delta TF$	-1 (-7)	-4 (-10)	-10 (-9)	-7 (-3)	13 (2)	
			Location 14			
$\Delta \delta OP_{corr}$	-8 (-26)	-22 (-22)	-80 (-24)	-165 (-22)	-136 (-13)	
$\Delta \delta TF$	-9 (-29)	-20 (-20)	—18 (—5)	-63 (-8)	-52 (-5)	
δ^2 H						
			Location 1			
δΟΡ	14	42	127	501	944	
δTF	12	35	97	327	839	
			Location 14			
δΟΡ	31	126	445	827	1084	
δTF	19	72	346	745	1040	
			Location 1			
$\Delta \delta TF$	-2 (-14)	-7 (-17)	-30 (-24)	-174 (-35)	-105 (-11)	
			Location 14			
$\Delta \delta TF$	-12 (-39)	-54 (-43)	-99 (-22)	-82 (-10)	-44 (-4)	
2						

Table 1. Quantile Transit Times of the Cumulative TTDs for Locations 1 and 14 Using δOP , δOP_{corr} , and δTF^a Quantile Transit Time of Cumulative TTD (days)

^aDifferences in transit time and percentage change (in brackets) shown for comparison of δOP with δOP_{corr} ($\Delta \delta OP_{corr}$) and of δOP with δTF ($\Delta \delta TF$).

of ungauged catchments by, e.g., utilizing catchment characteristics to estimate MTTs [*Hrachowitz et al.*, 2013b], it is very important to use TF in forested catchments. Therefore, we recommend using δ TF instead of δ OP to derive improved TTD estimates in forest hydrological studies. However, if δ TF measurement is not possible, stable isotope driven TTD studies might benefit from an empirical calibration of δ OP_{corr} with the initial assumption of an overall enrichment in the isotopic composition of δ OP in temperate forests.

Our findings are relevant for forested catchments where isotopic fractionation due to interception occurs and is not implicitly considered in the model. This is regardless of catchment size when using spatially uniform input data, as is often done in the convolution integral approach [*McGuire and McDonnell*, 2006]. In the case of partially forested catchments, land cover information could be used to weigh TF and OP.

4. Conclusions

We compared δTF and δOP in TTD modeling for the spruce covered Wüstebach catchment in Germany. Calculated transit times were reduced when using TF for both tracers $\delta^{18}O$ and $\delta^{2}H$ by up to 4 months (119 days). The difference in cumulative TTD was 7.5%. While the quality of the stream isotope simulations varied significantly within TRANSEP, the results were always weaker when using δOP . We conclude that consideration of the effects of interception on δOP is important for accurate TTD estimation of forested catchments. This demands the inclusion of TF measurements in the design of hydrological sampling campaigns in forested catchments. Our results further suggest that if no TF measurements are available, a simple correction of precipitation data could lead to improved isotope modeling results. More studies are needed that investigate the actual effects of canopy-induced changes on δOP on hydrological modeling results, e.g., under different vegetation types or climatic conditions, and for different temporal resolutions.

Acknowledgments

We gratefully acknowledge the support by the SFB-TR32 "Patterns in Soil-Vegetation-Atmosphere Systems: Monitoring, Modelling, and Data Assimilation" funded by the Deutsche Forschungsgemeinschaft (DFG) and **TERENO** (Terrestrial Environmental Observatories) funded by the Helmholtz-Gemeinschaft. Holger Wissel, Werner Küpper, Rainer Harms, Ferdinand Engels, Leander Fürst, and Sebastian Linke are thanked for supporting the isotope analysis, sample collection, and the ongoing maintenance of the experimental setup. Clemens Drüe is thanked for supplying the data and information for the University of Trier throughfall sampling system. The data used in this study can be acquired from the corresponding author. We thank two anonymous reviewers and the Editor who helped to considerably improve this paper.

The Editor thanks two anonymous reviewers for their assistance in evaluating this paper.

References

- Abbaspour, K. C., R. Schulin, and M. T. van Genuchten (2001), Estimating unsaturated soil hydraulic parameters using ant colony optimization, Adv. Water Resour., 24(8), 827–841.
- Allen, S. T., J. R. Brooks, R. F. Keim, B. J. Bond, and J. J. McDonnell (2014), The role of pre-event canopy storage in throughfall and stemflow by using isotopic tracers, *Ecohydrology*, 7, 858–868, doi:10.1002/eco.1408.
- Asano, Y., T. Uchida, and N. Ohte (2002), Residence times and flow paths of water in steep unchannelled catchments, Tanakami, Japan, J. Hydrol., 261(1–4), 173–192.
- Berman, E. S. F., M. Gupta, C. Gabrielli, T. Garland, and J. J. McDonnell (2009), High-frequency field-deployable isotope analyzer for hydrological applications, *Water Resour. Res.*, 45, W10201, doi:10.1029/2009WR008265.
- Birkel, C., S. M. Dunn, D. Tetzlaff, and C. Soulsby (2010), Assessing the value of high-resolution isotope tracer data in the stepwise development of a lumped conceptual rainfall-runoff model, *Hydrol. Processes*, 24(16), 2335–2348.
- Birkel, C., D. Tetzlaff, S. M. Dunn, and C. Soulsby (2011), Using lumped conceptual rainfall-runoff models to simulate daily isotope variability with fractionation in a nested mesoscale catchment, Adv. Water Resour., 34(3), 383–394.
- Birkel, C., C. Soulsby, D. Tetzlaff, S. Dunn, and L. Spezia (2012), High-frequency storm event isotope sampling reveals time-variant transit time distributions and influence of diurnal cycles, *Hydrol. Processes*, 26(2), 308–316.
- Bogena, H. R., et al. (2014), A terrestrial observatory approach to the integrated investigation of the effects of deforestation on water, energy, and matter fluxes, Sci. China Earth Sci., 57, 1–15.
 - Botter, G., E. Bertuzzo, and A. Rinaldo (2011), Catchment residence and travel time distributions: The master equation, *Geophys. Res. Lett.*, 38, L11403, doi:10.1029/2011GL047666.

Brodersen, C., S. Pohl, M. Lindenlaub, C. Leibundgut, and K. von Wilpert (2000), Influence of vegetation structure on isotope content of throughfall and soil water, *Hydrol. Processes*, 14(8), 1439–1448.

- Brooks, J. R., H. R. Barnard, R. Coulombe, and J. J. McDonnell (2010), Ecohydrologic separation of water between trees and streams in a Mediterranean climate, *Nat. Geosci.*, 3(2), 100–104.
- Calderon, H., and S. Uhlenbrook (2014), Characterising the climatic water balance dynamics and different runoff components in a poorly gauged tropical forested catchment, Nicaragua, *Hydrol. Sci. J.*, doi:10.1080/02626667.2014.964244.
- Cappa, C. D., M. B. Hendricks, D. J. DePaolo, and R. C. Cohen (2003), Isotopic fractionation of water during evaporation, J. Geophys. Res., 108(D16), 4525, doi:10.1029/2003JD003597.
- Celle-Jeanton, H., R. Gonfiantini, Y. Travi, and B. Sol (2004), Oxygen-18 variations of rainwater during precipitation: Application of the Rayleigh model to selected rainfalls in Southern France, J. Hydrol., 289(1–4), 165–177.
- Criss, R. E., and W. E. Winston (2008), Do Nash values have value? Discussion and alternate proposals, *Hydrol. Processes*, 22(14), 2723–2725. Dewalle, D. R., and B. R. Swistock (1994), Differences in O-18 content of throughfall and rainfall in hardwood and coniferous forests, *Hydrol. Processes*, 8(1), 75–82.
- Etmann, M. (2009), Dendrologische Aufnahmen im Wassereinzugsgebiet Oberer Wüstebach anhand verschiedener Mess- und Schätzverfahren, MS thesis, Institut für Landschaftsökologie, Univ. of Münster, Münster, Germany.
- Gonfiantini, R. (1978), Standards for stable isotope measurements in natural compounds, *Nature*, 271(5645), 534–536.
- Graf, A., H. R. Bogena, C. Drüe, H. Hardelauf, T. Pütz, G. Heinemann, and H. Vereecken (2014), Spatiotemporal relations between water budget components and soil water content in a forested tributary catchment, *Water Resour. Res., 50*, 4837–4857, doi:10.1002/ 2013WR014516.
- Harman, C. J. (2015), Time-variable transit time distributions and transport: Theory and application to storage-dependent transport of chloride in a watershed, *Water Resour. Res.*, 51(1), 1–30, doi:10.1002/2014WR015707.
- Heidbüchel, I., P. A. Troch, S. W. Lyon, and M. Weiler (2012), The master transit time distribution of variable flow systems, *Water Resour. Res.*, 48, W06520, doi:10.1029/2011WR011293.
- Hrachowitz, M., C. Soulsby, D. Tetzlaff, J. J. C. Dawson, and I. A. Malcolm (2009), Regionalization of transit time estimates in montane catchments by integrating landscape controls, *Water Resour. Res.*, 45, W05421, doi:10.1029/2008WR007496.
- Hrachowitz, M., H. Savenije, T. A. Bogaard, D. Tetzlaff, and C. Soulsby (2013a), What can flux tracking teach us about water age distribution patterns and their temporal dynamics?, *Hydrol. Earth Syst. Sci.*, 17(2), 533–564.
- Hrachowitz, M., et al. (2013b), A decade of predictions in ungauged basins (PUB)a review, Hydrol. Sci. J., 58(6), 1198–1255.
- Kato, H., Y. Onda, K. Nanko, T. Gomi, T. Yamanaka, and S. Kawaguchi (2013), Effect of canopy interception on spatial variability and isotopic composition of throughfall in Japanese cypress plantations, J. Hydrol., 504, 1–11.
- Kubota, T., and Y. Tsuboyama (2003), Intra- and inter-storm oxygen-18 and deuterium variations of rain, throughfall, and stemflow, and two-component hydrograph separation in a small forested catchment in Japan, J. For. Res., 8(3), 179–190.
- Lyon, S. W., S. L. E. Desilets, and P. A. Troch (2009), A tale of two isotopes: Differences in hydrograph separation for a runoff event when using delta D versus delta O-18, *Hydrol. Processes*, 23(14), 2095–2101.
- McGuire, K. J., and J. J. McDonnell (2006), A review and evaluation of catchment transit time modeling, J. Hydrol., 330(3–4), 543–563.
- Nash, J. E., and J. V. Sutcliffe (1970), River flow forecasting through conceptual models: Part I—A discussion of principles, J. Hydrol., 10(3), 282–290.
- Peng, H. H., C. Y. Zhao, Z. D. Feng, Z. L. Xu, C. Wang, and Y. Zhao (2014), Canopy interception by a spruce forest in the upper reach of Heihe River basin, Northwestern China, *Hydrol. Processes*, 28(4), 1734–1741.

Richter, F. (2008), Bodenkarte zur Standorterkundung. Verfahren Quellgebiet Wüstebachtal (Forst), Geologischer Dienst Nordrhein-Westfalen, Krefeld, Germany.

- Rinaldo, A., K. J. Beven, E. Bertuzzo, L. Nicotina, J. Davies, A. Fiori, D. Russo, and G. Botter (2011), Catchment travel time distributions and water flow in soils, *Water Resour. Res.*, 47, W07537, doi:10.1029/2011WR010478.
- Saxena, R. K. (1986), Estimation of canopy reservoir capacity and O-18 fractionation in throughfall in a pine forest, Nord. Hydrol., 17(4–5), 251–260.
- Stockinger, M. P., H. R. Bogena, A. Lücke, B. Diekkrüger, M. Weiler, and H. Vereecken (2014), Seasonal soil moisture patterns: Controlling transit time distributions in a forested headwater catchment, *Water Resour. Res., 50*, 5270–5289, doi:10.1002/2013WR014815.
- Tetzlaff, D., J. Seibert, and C. Soulsby (2009), Inter-catchment comparison to assess the influence of topography and soils on catchment transit times in a geomorphic province; the Cairngorm mountains, Scotland, *Hydrol. Processes*, 23(13), 1874–1886.
- Timbe, E., D. Windhorst, P. Crespo, H. G. Frede, J. Feyen, and L. Breuer (2014), Understanding uncertainties when inferring mean transit times of water trough tracer-based lumped-parameter models in Andean tropical montane cloud forest catchments, *Hydrol. Earth Syst. Sci.*, 18(4), 1503–1523.

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

Windhorst, D., P. Kraft, E. Timbe, H. G. Frede, and L. Breuer (2014), Stable water isotope tracing through hydrological models for disentangling runoff generation processes at the hillslope scale, *Hydrol. Earth Syst. Sci., 18*(10), 4113–4127.

World Meteorological Organization (2008), Guide to Meteorological Instruments and Methods of Observation, 7th ed., World Meteorol. Organ., Geneva, Switzerland.

Zacharias, S., et al. (2011), A network of terrestrial environmental observatories in Germany, Vadose Zone J., 10(3), 955–973.