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Accounting for seasonal isotopic patterns of forest canopy intercepted precipitation in streamflow modeling

Michael P. Stockinger *, Andreas Lücke, Harry Vereecken, Heye R. Bogena

Forschungszentrum Jülich GmbH, Institute of Bio- and Geosciences, Agrosphere Institute (IBG-3), Wilhelm-Johnen-Straße, 52425 Jülich, Germany

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A B S T R A C T

Forest canopy interception alters the isotopic tracer signal of precipitation leading to significant isotopic differences between open precipitation (δOP) and throughfall (δTF). This has important consequences for the tracer-based modeling of streamwater transit times. Some studies have suggested using a simple static correction to δOP by uniformly increasing it because δTF is rarely available for hydrological modeling. Here, we used data from a 38.5 ha spruce forested headwater catchment where three years of δOP and δTF were available to develop a data driven method that accounts for canopy effects on δOP. Changes in isotopic composition, defined as the difference δTF-δOP, varied seasonally with higher values during winter and lower values during summer. We used this pattern to derive a corrected δOP time series and analyzed the impact of using (1) δOP, (2) reference throughfall data (δTF_{ref}) and (3) the corrected δOP time series (δOP_{Sine}) in estimating the fraction of young water (F_{yw}), i.e., the percentage of streamflow younger than two to three months. We found that F_{yw} derived from δOP_{Sine} came closer to δTF_{ref} in comparison to δOP. Thus, a seasonally-varying correction for δOP can be successfully used to infer δTF where it is not available and is superior to the method of using a fixed correction factor. Seasonal isotopic enrichment patterns should be accounted for when estimating F_{yw} and more generally in catchment hydrology studies using other tracer methods to reduce uncertainty.

1. Introduction

Forest canopy interception increases the time for precipitation to reach the forest floor and reduces rainfall amounts due to evaporation. Additionally, evaporation also changes the isotopic composition of precipitation by isotopic fractionation, usually enriching the remaining water (Cappa et al., 2003, Dewalle and Swistock, 1994). A recent review summarized 24 interception studies and found a mean enrichment of around 0.2‰ for oxygen-18, with several studies exceeding mean enrichments of 0.5‰ (Allen et al., 2016). Although seldom, even isotopic depletion of throughfall was observed. These studies did not find temporal stability of interception-induced isotopic changes (Allen et al., 2014; Brodersen et al., 2000).

The isotopic difference of precipitation above (open precipitation, OP) and below the canopy (throughfall, TF) becomes important when using the stable isotopes of water (δ^2H and $\delta^{18}O$) of OP (δOP) as input data to hydrological models assuming strictly conservative behavior. So far many studies focused on describing stable isotope patterns of TF (δTF) (Ikawa et al., 2011; Pichon et al., 1996; Xu et al., 2014), but only few used δTF in hydrological modeling (Gibson et al., 2000; Fitzgerald et al., 2003; Liu et al., 2015). However, previous studies on hydrograph separation (Kubota and Tsuboyama, 2003) and on transit time distribution estimation (Stockinger et al., 2015) have revealed significant differences when using δOP or δTF for forested locations. Both studies demonstrate that the use of biased input data can lead to misinterpretation of catchment runoff generation processes. A skewed estimate of the amount and timing of the arriving water may impact the prediction of nutrient and dissolved organic matter transport to groundwater and streams (Bachmair et al., 2009; Gottselig et al., 2014).

δTF is seldom available at a specific location due to technical, administrative and/or financial restrictions. Therefore, several correction methods were presented in literature to quantify the effect of canopy interception on δOP. Stockinger et al. (2014) and Calderon and Uhlenbrook (2014) proposed a constant correction factor of 0.5‰ and 1.4‰, respectively. A more complex approach of weighing measured open precipitation, deciduous forest and coniferous forest throughfall isotope data based on land use percentages was suggested by Stockinger et al. (2016). However, a simple shift of isotopic data to account for enrichment might not

* Corresponding author at: Forschungszentrum Jülich GmbH, Agrosphere Institute (IBG-3), Wilhelm-Johnen-Straße, D-52425, Germany.
E-mail address: m.stockinger@fz-juelich.de (M.P. Stockinger).

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be adequate because temporal differences in the δOP to δTF relationship may occur on different timescales, e.g. annual, seasonal or event.

One emerging tool where interception effects could have important effects is the fraction of young water (F_{yw}). F_{yw} has been proposed as a measure for characterizing the fast flow component of water transport through a catchment (Kirchner, 2016). It represents the percentage of water in streamflow that is younger than a certain threshold age τ_{yw} and is derived from tracer data. Interception effects on F_{yw} cannot be corrected with the constant correction factor applied in previous studies, as it uniformly shifts all data points towards more positive values. This in turn will not change the parameters necessary to calculate F_{yw} (the amplitude and phase shift of a fitted sine wave; see also Section 2 of this study).

In the present study we analyzed temporal δ^{18}O patterns of a three-year time series of OP and TF in a coniferous and a deciduous forest. Our results suggest that a seasonally variable correction of δOP data is needed and we therefore developed a respective correction method. We calculated F_{yw} using the corrected δOP and compared this to F_{yw} derived from δTF (the reference) and the uncorrected δOP. F_{yw} results were compared to test if our correction improves F_{yw} results towards the reference.

2. Methods

2.1. Study site

Coniferous forest TF and OP data was obtained from the Wüstebach headwater catchment (38.5 ha) of the Erkensruhr River, Germany, which is part of the Lower Rhine/Eifel Observatory of the Terrestrial Environmental Observatories (TERENO) network (Zacharias et al., 2011). Elevation ranges from 595 to 628 m asl., with the climate being humid temperate with mean annual precipitation of 1107 mm (1961–1990) and a mean annual temperature of 7 °C (Zacharias et al., 2011). 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). Soil types of cambisol and planosol/cambisol are found on hillslopes, whereas gleysols, histosols and planosols are found in the riparian zone. During the time of our investigation most of the catchment was homogeneously covered with Norway spruce (*Picea abies*) and Sitka spruce (*Picea sitchensis*) (Etmann, 2009), while 8 ha (~21%) was clear-cut approximately at the start of the time series.

Deciduous forest TF was obtained from the station "Im Brand" which is a natural forest reserve. The station is located at 480 m a.s.l. in the Erkensruhr catchment (Fig. 1) and lies about 7.5 km north of the Wüstebach catchment. The site is covered by 65–80 years old beech trees. The climate, soil and bedrock characteristics are comparable to the Wüstebach site. More detailed descriptions of the Erkensruhr catchment can be found in (Stockinger et al., 2016) and (Cornelissen et al., 2016).

2.2. Measured data

Weekly isotope data (δ^{18}O) relative to Vienna Standard Mean Ocean Water (VSMOW) (Brand et al., 2014) and volume data of TF and OP were collected from April 12, 2013 to March 5, 2016 (Supplement Fig. S1). Due to collinearity, only δ^{18}O was used in the analysis but no δ^{2}H. At each location TF was collected with six samplers (RS200, UMS GmbH, Germany) while OP was collected at Wüstebach with two samplers of the same design. The samplers consisted of 1.80 m vertical pipes which were buried approximately 30 cm in soil in a distance of 2 m to each other and 2 m from tree trunks. A mesh-protected funnel with a diameter of 20 cm was installed on top which led precipitation water via an approximately 2 cm diameter plastic tube to a collection bottle which was placed inside the samplers. Those measures were taken in order to prevent evaporative loss and thus isotopic fractionation of the collected water. The system was already shown to be reliable in this context as well as representative for the forested Wüstebach area (Stockinger et al., 2015). The TF and OP samples were volume-weighed on a weekly basis to create a TF and OP precipitation input time series, respectively. The TF data of Wüstebach used in this study partly contains the TF data already presented by Stockinger et al. (2015) and in comparison doubles the time series length from 1.5 to 3 years.

In addition, we used rain- and snowfall data from the meteorological station Kalterherberg (German Weather Service, station number 80115, 535 m asl.) which is located nine km northwest of Wüstebach. Rainfall data of 1 h intervals in 0.1 mm increments was used to volume-weigh isotope values during the calculation of F_{yw}. Finally, we used temperature data of the meteorological station Schöneseiffen (620 m asl., 3 km to the northeast) to further analyze isotopic Oxygen-18 enrichment patterns.

F_{yw} was calculated time-weighed by further using weekly isotope data from stream water grab samples taken at the Wüstebach runoff gauging station (Fig. 1). The grab samples were volume-weighed according to runoff at the moment of sample collection. They are mostly representative of base flow conditions.

Water isotopic analysis was carried out using laser-based cavity ringdown spectrometers (models L2120-i and L2130-i, Picarro). Internal standards calibrated against VSMOW, Standard Light Antarctic Precipitation (SLAP2) and Greenland Ice Sheet Precipitation (GISP) were used for calibration and to ensure long-term stability of analyses. The precision of the analytical system was ≤0.1 ‰ for δ^{18}O.

2.3. Pattern analysis and young water fractions

The isotopic change Δδ due to forest canopy interception in Wüstebach was calculated as the difference δTF-δOP. We assumed that the δOP measurements at this location were representative for the whole Erkensruhr catchment (Fig. 1). However, due to small scale isotopic differences the calculation of Δδ for station "Im Brand" was not possible.

Upon visual inspection a seasonal pattern in Δδ was apparent which was then fitted to a sine wave function (Fig. 2, Eq. (1)). By adding the respective values of this sine wave to each δOP data point we derived δOP_{Sine} which better represents δTF. To verify this, we calculated a reference F_{yw} and compared it to F_{yw} results based on δOP (assumed to give less similar results to the reference) and δOP_{Sine} (assumed to give more similar results to the reference). The reference F_{yw} was derived by weighing δTF and δOP according to land-use percentages (forested: 79%, deforested: 21%, Fig. 1), which will from now on be referred to as δTF_{ref}.

In the following, we briefly explain the calculation of F_{yw} (for a detailed description we refer to Kirchner (2016)). The method assumes a conservative tracer passing through the catchment, i.e., the only change the tracer undergoes from input to output solely happens due to hydrological processes connected with water flow. Usually, precipitation (input) and streamflow (output) are used as their stable water isotopes show an annual sinusoidal signal.

We used multiple linear regressions with the sine and cosine components as the independent variables to fit sine waves to the tracer input and output signals (Eq. (1)). The respective amplitudes (A_p and A_s) and phase shifts (φ_P and φ_S) were subsequently calculated (Eq. (2)) (Kirchner, 2016; Stockinger et al., 2016):

$$C_P(t) = a_P \cos(2\pi ft) + b_P \sin(2\pi ft) + k_P,$$

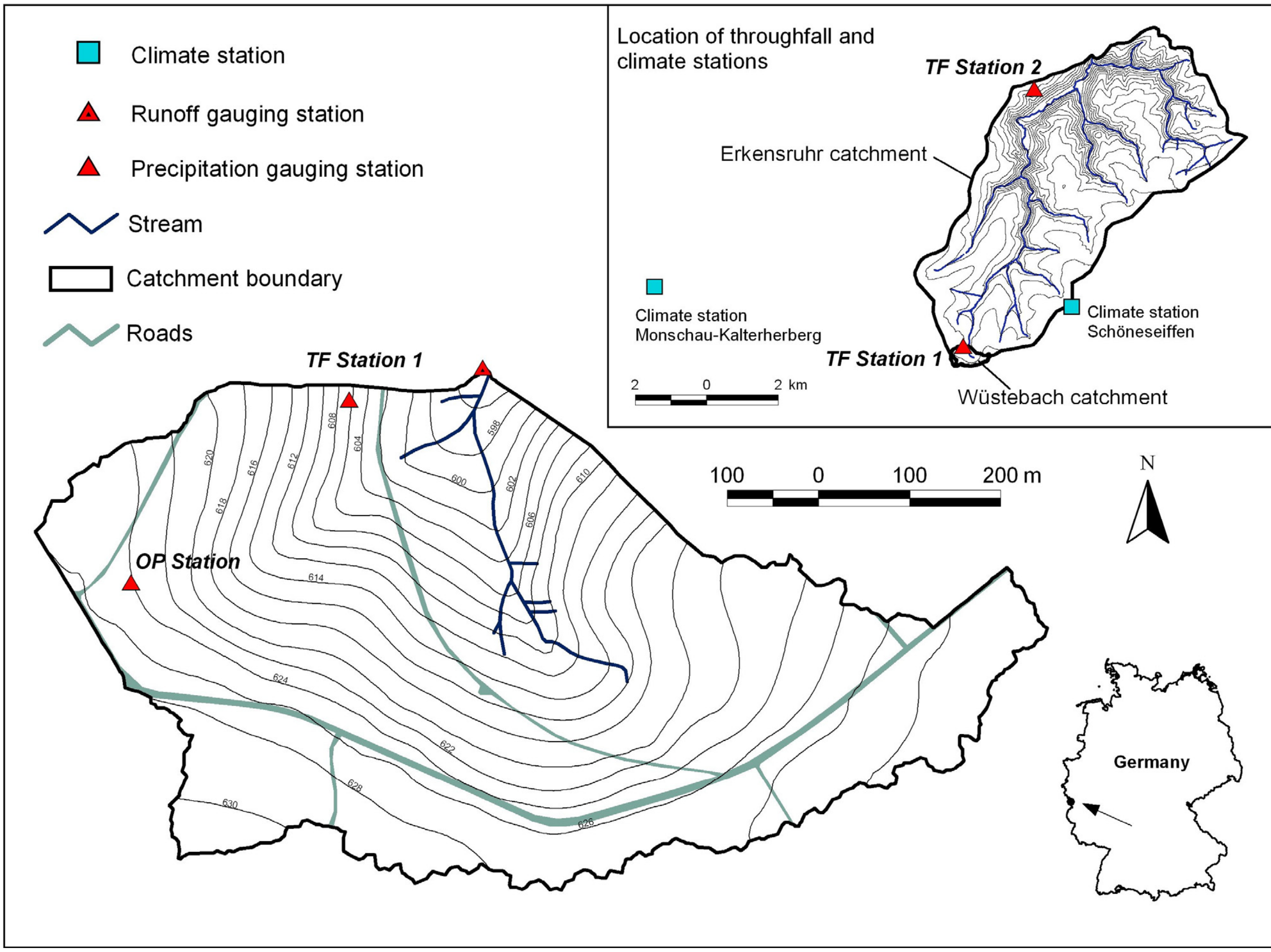

Fig. 1. Map showing the Wüstebach and Erkensruhr catchments as well as the used monitoring stations. OP Station is the open precipitation collection site, while TF Station 1 is the coniferous forest throughfall station and TF Station 2 is the deciduous forest throughfall station "Im Brand".

$$C_S(t) = a_S \cos(2\pi ft) + b_S \sin(2\pi ft) + k_S \quad (1)$$

$$A_P = \sqrt{a_P^2 + b_P^2},\ A_S = \sqrt{a_S^2 + b_S^2},$$
$$\varphi_P = \tan^{-1}\left(\frac{a_P}{b_P}\right),\ \varphi_S = \tan^{-1}\left(\frac{a_S}{b_S}\right) \quad (2)$$

with $C_P(t)$ and $C_S(t)$ being the tracer signal in precipitation and streamflow at time t, f the frequency of the fitted sine wave, a and b the regression coefficients, and k_P and k_S represent the vertical shift of the sine wave. The frequency was set to 1/8766 h (365.25 × 24, i.e., 1 per year) due to the annual seasonal behavior of precipitation and streamflow isotopes. The goodness-of-fit was calculated using the coefficient of determination (R^2). Due to the high variability in isotopic input data, R^2 was calculated with the quarterly means of the measurements compared to the sine wave fits.

The amplitudes were used to directly estimate F_{yw} by A_s/A_p (we term this the "simple calculation method"). Alternatively, we used the phase shifts to find the shape and scale parameters α and β of a lower incomplete gamma function Γ(α,β) for F_{yw} estimation (complex method). Kirchner (2016) tested the F_{yw} method for α values between 0.2 and 2. Γ(α,β) does not represent a valid transit time distribution for the catchment (Kirchner, 2016) but can be used to derive the threshold age τ_{yw} that defines the "young" in the fraction of young water. With τ_{yw}, α and β the fraction of water in streamflow which is younger than τ_{yw} was calculated:

$$F_{yw} = \Gamma(\tau_{yw}, \alpha, \beta) = \int_{\tau=0}^{\tau_{yw}} \frac{\tau^{\alpha-1}}{\beta^{\alpha}\Gamma(\alpha)} e^{-\frac{\tau}{\beta}} d\tau \quad (3)$$

We used three different calculation methods to estimate the uncertainty of F_{yw} (see Section 3.3): (a) the simple F_{yw} calculation, (b) the complex F_{yw} calculation and, (c) splitting up the time series into annual subsets to calculate F_{yw}, based on the following reasoning:

Fitting a single sine wave function to a multi-year time series requires a stable sinusoidal signal. Thus, we visually inspected the three-month running average of precipitation and streamflow isotope data (similar to Pearce et al. (1986), Supplement Fig. S2). We found a time-varying sinusoidal signal and initially split the 3-year data set into three individual years to account for this effect in calculating F_{yw}. However, after testing we found that splitting up the time series in hydrological years (November 1 to October 30) leads to a better performance of the method. Thus, additionally to using one single sine wave function for the complete time series, we shortly present and discuss results obtained by the two hydrological years separation, while giving more details and results of the initial split-up into three years in the Supplementary Material.

3. Results and discussion

3.1. Isotopic data

δOP ranged from −17.97 to −3.18‰ with a weighted mean of −8.76‰ (Fig. 6). δTF of the coniferous forest Wüstebach had a similar range but a weighted mean value enriched by 0.51‰ (−17.76 to −3.04‰ and weighted mean of −8.25‰), while δTF of the decid-

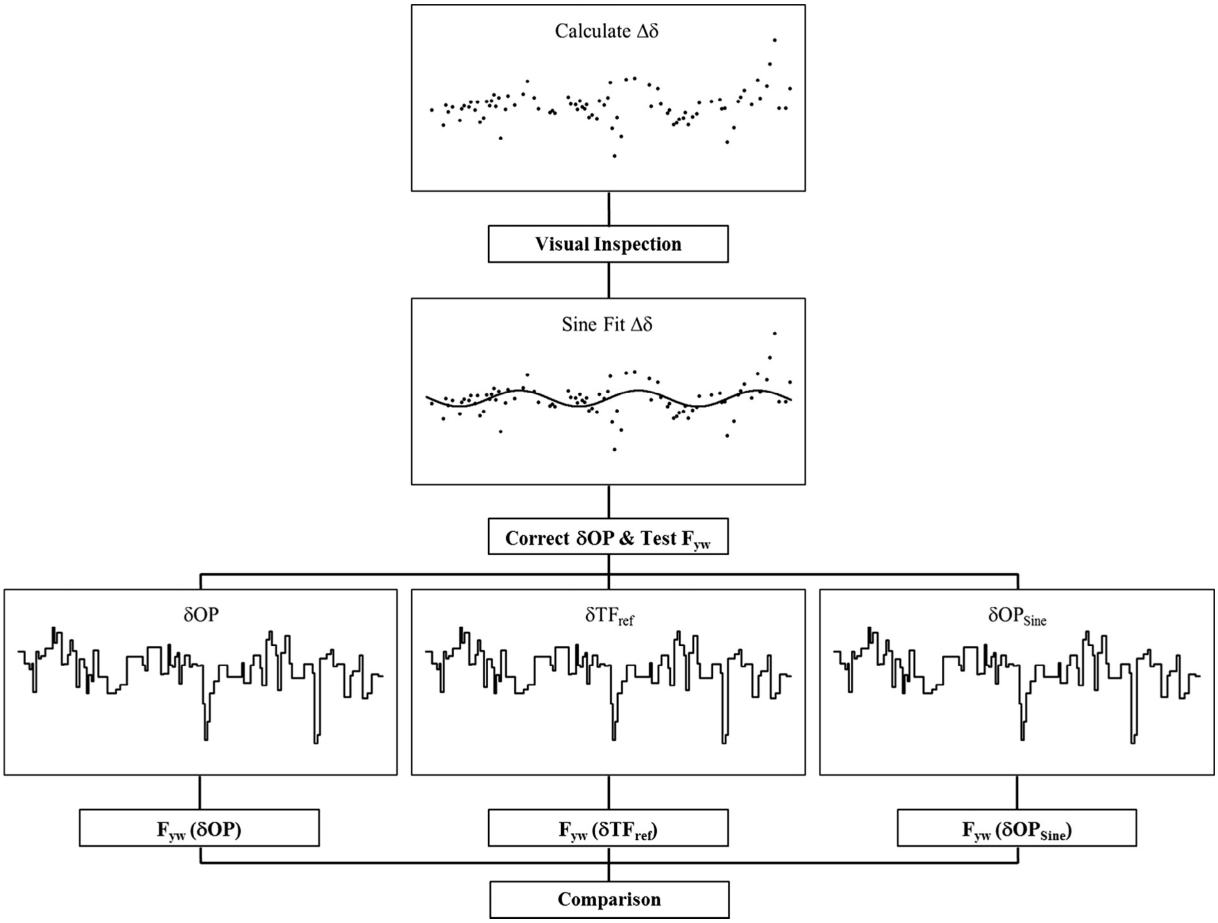

Fig. 2. Workflow showing the initial Δδ data set which was visually inspected assuming a sine wave characteristic. Subsequently a sine wave was fitted and used to transform δOP to δOP_{Sine}. After this, the three inputs δOP, δTF_{ref} and δOP_{Sine} were used to calculate the fraction of young water F_{yw} and the results compared.

uous forest station "Im Brand" ranged from −19.49 to −3.54‰ with a weighted mean of −8.48‰. The isotopic change Δδ was between +2.94 and −1.70‰. Streamflow ranged from −8.74 to −7.78‰ with a flow-weighted mean of −8.40‰.

The observed enrichment of δTF relative to δOP by 0.51‰ coincides well with the previously found constant correction value of 0.5‰ of Stockinger et al. (2014) for the same location. In their study the value of 0.5‰ was found by inverse modeling. With the now available three years of TF measurement this theoretical value can be substantiated with empirical data. Interestingly, the deciduous forest δTF differed from δOP by only 0.28‰. This relatively small difference may be due to the loss of foliage in winter time, which generally reduces interception capacity of trees (Herbst et al., 2008; Nakai et al., 1993).

The relatively small spatial extent of our TF sampling system might raise concerns regarding the representativeness of the collected samples. Following recommendations of Zimmermann et al. (2016) an average error of 10% can be approximated considering the homogeneity of the Wüstebach forest plantation and the average TF volume of 30 mm. This relatively small error will have only a minor effect on δTF. In addition, Stockinger et al. (2015) compared the TF sampling system with an independently operated 50 m distant trough collection system and found good agreement in measured TF.

3.2. Isotopic enrichment patterns

The monthly average difference of δTF to δOP showed a seasonal pattern with larger enrichment in the winter months December to March (average enrichment of +0.84‰) and lower but increasing enrichment from April to November (average enrichment of +0.11‰, Fig. 3). Isotopic depletion mainly occurred during spring and summer and could have been a result of mixing with residual water in the canopy (Allen et al., 2014) or the potential complete evaporation of intercepted rainfall with more positive isotope values than the other events of that sampling week. Similar results were obtained by Claassen and Downey (1995) who found higher enrichment in δTF of an evergreen forest during winter months. This is surprising at first, as one would expect higher enrichment during times of increased energy input and thus increased interception losses, i.e., during summer. Interception loss did indeed increase during spring and summer in contrast to winter times (Fig. 4). However, October and December still retained high interception losses, which according to Herbst et al. (2008) can be possible due to e.g., higher wind speeds or changed aerodynamic properties of the canopy during leafless times. The last explanation must be ruled out as the Wüstebach is a coniferous forest. Another possible source for aerodynamic property changes is the buildup of snow pack in the canopy. Nevertheless, a pattern of higher interception during summer does exist but cannot explain higher Δδ values and thus higher TF enrichment at low temperatures during winter. No correlation was found between interception loss and Δδ, which has often been observed in other studies. It has been argued that this missing correlation is an indication that evaporation might not be the dominant process controlling the isotope signal of δTF (Allen et al., 2016).

The seasonal behavior of Δδ can partly be explained by snowfall and the temperature-dependence of isotope fractionation. We found

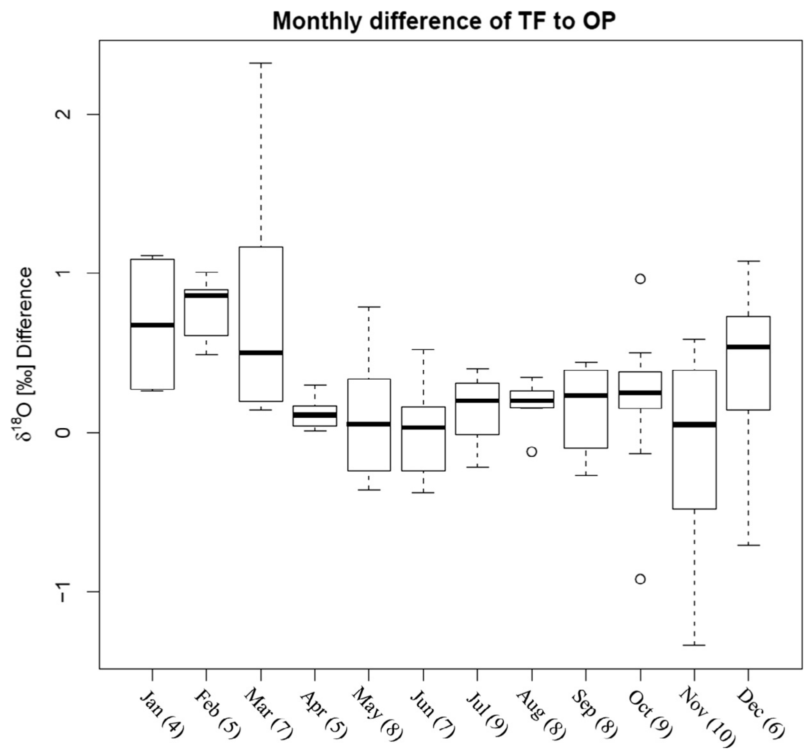

Fig. 3. Boxplot of monthly differences of $\delta^{18}O$ isotope values of δTF to δOP of the coniferous forest location Wüstebach. Whiskers are the upper and lower 1.5 interquartile range and circles are outlier values. The number of data points for each month is given in the brackets on the horizontal axis.

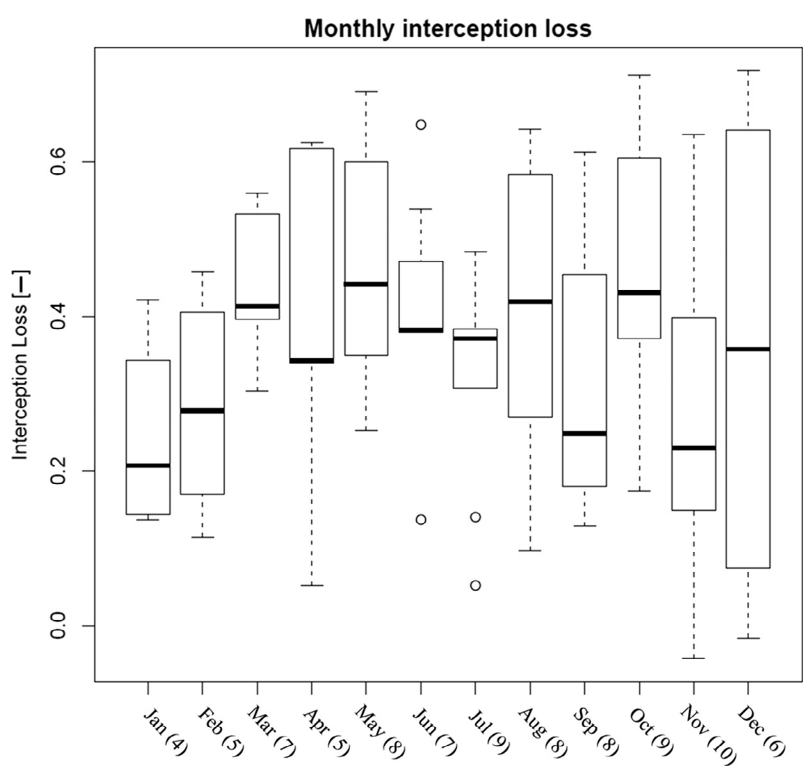

Fig. 4. Relative monthly interception loss of the spruce-forest covered Wüstebach catchment. Whiskers are the upper and lower 1.5 interquartile range and circles are outlier values. The number of data points for each month is given in the brackets on the horizontal axis.

that Δδ values that were influenced by snow occurrence tended to be larger than the uninfluenced ones (Fig. 5). First, forest canopy intercepted snow has an increased surface area subjected to sublimation compared to snow falling on the ground (Claassen and Downey, 1995). Additionally, the time that snow is intercepted on forest canopy is longer than that of rainfall (Lundberg and Halldin, 2001).

Second, isotopic fractionation is temperature-dependent, such that it decreases with increasing temperatures (Mook, 2000). Third, we assume that enriched snowmelt will more likely reach the forest floor than intercepted summer precipitation because of evaporation effects. Combined, this should lead to higher isotopic fractionation during winter periods in the Wüstebach forest.

δTF measured at the deciduous forest station "Im Brand" was used to test the hypothesis of snow contributing to the Δδ pattern observed at Wüstebach (Fig. 6). For this we assumed δOP of "Im Brand" to be similar in amplitude (not in values) to δOP of Wüstebach (no on-site measurement of δOP at "Im Brand"), as no isotopic gradient was found for this region (Stockinger et al., 2016). The δTF sine wave of the coniferous forest showed a larger difference to the δOP sine wave than the δTF sine wave of the deciduous forest (difference in amplitude of 0.43‰ and 0.14‰, respectively). This indicates that enrichment rates are smaller for leafless times as the difference was most notably during winter months. Thus, it corroborates our assumption that canopy-intercepted snow played a role in forming the seasonal pattern observed at Wüstebach.

Alternatively, one could argue that during winter snow accumulates in the funnel of the unheated TF samplers, leading to long exposure of snow to sublimation. However, in that case the OP samplers should be more affected as they receive more snowfall and are more exposed to global radiation and wind, and thus more prone to sublimation. Consequently, Δδ should be lower in winter compared to summer, as it is calculated as δTF-δOP. We are confident that snow buildup in the funnel of the TF samplers is not the driving force for higher Δδ values during winter since we found an increase of Δδ in winter.

Ultimately, it is not the intention of this study to fully explain why the seasonal behavior occurred, but to use it to appropriately correct δOP. The complexity of the undertaking of physically explaining Δδ was shown in the review study of Allen et al. (2016), highlighting different effects on Δδ as well as future research needs. Important in the context of this study is the fact that the seasonal behavior of Δδ changes the amplitude of δOP during canopy passage before it reaches the soil and enters the catchment as δTF (Fig. 6, Table 1). As shown in the Section 3.3, this has an effect on the estimation of F_{yw}.

3.3. Fraction of young water

Isotope input data, the respective sine wave fits as well as Δδ for precipitation are shown in Fig. 6 while Fig. 7 shows input data and the respective sine wave fit for Wüstebach streamflow. The parameters of all sine waves are given in Table 1.

The F_{yw} method developed by Kirchner (2016) assumes that a conservative tracer is used. However, beside canopy interception modifications of the stable isotope signal in soil (Rothfuss et al., 2015) and open water evaporation in the stream (Maheu et al., 2014) are possible. Every stable isotope tracer application could potentially suffer under these short-comings. We cannot fully exclude further isotopic changes of input data past canopy passage due to the lack of more detailed information.

All α parameters of the gamma distributions except one ($\alpha = 0.11$) were within the range investigated by Kirchner (2016). We deemed this outlier insignificant for results as the simplified calculation of F_{yw} only considers the amplitudes of the fitted sine waves. The thus obtained F_{yw} value is independent from the α parameter and a good reference for the validity of F_{yw} calculated with α in the more complex method. The very close resemblance of both F_{yw} indicates the reliability of the calculation with $\alpha = 0.11$.

3.3.1. Calculations using the whole time series

The sine wave fits of δTF_{ref}, δOP, δOP_{Sine}, Δδ and the stream had quite low R^2 with 1×10^{-6}, 0.07, 0.02, 0.51 and 0.30, which was to be expected in the case of a time-varying sinusoidal tracer signal. The low R^2 can be explained by few isotopically highly negative rainfall inputs (Fig. 6, red arrows). The amplitudes and phase shifts of δOP_{Sine} were close to the ones of δTF_{ref} but the amplitudes and phase shifts of δOP showed larger differences to δTF_{ref} (Table 1). F_{yw} and τ_{yw} showed clear improvements: δOP had 8.5–8.8% of streamwater being younger than 46 days and was far off from δTF_{ref} with 12.5–12.6% of streamwater being younger than 39 days (Table 2). δOP_{Sine} clearly improved on this with 10.7–11.0% being younger than 44 days.

We tested splitting up the time series to adapt to the time-varying sinusoidal signal and improve R^2 due to the low R^2 of the fitted sine waves using the whole time series. In the following we test and shortly discuss how splitting the three-year tracer time

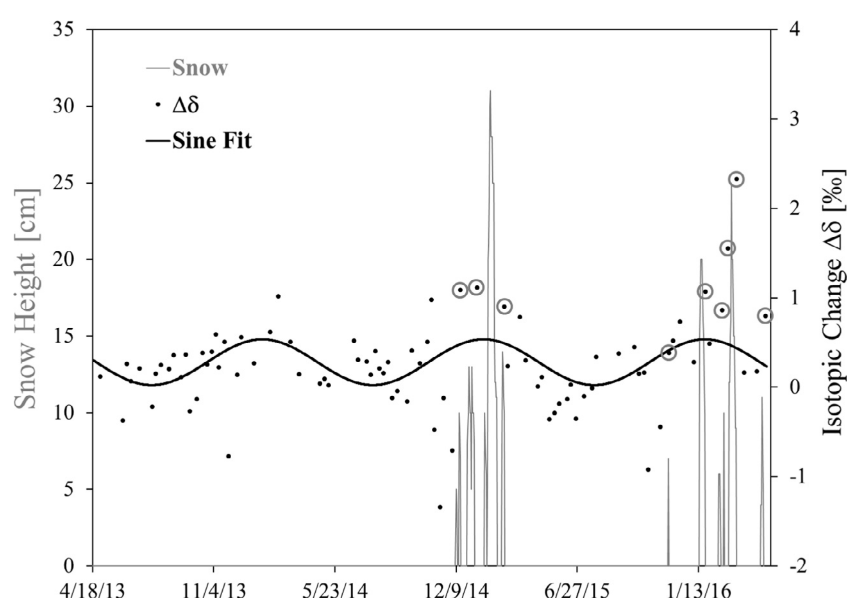

Fig. 5. Snow height at meteorological station Kalterherberg and isotopic changes of throughfall samples (Δδ = δTF-δOP) at Wüstebach. Δδ was fitted with a sine waves of R^2 = 0.51 (Sine Fit). Circled Δδ values are measurements after complete melt of the snow cover.

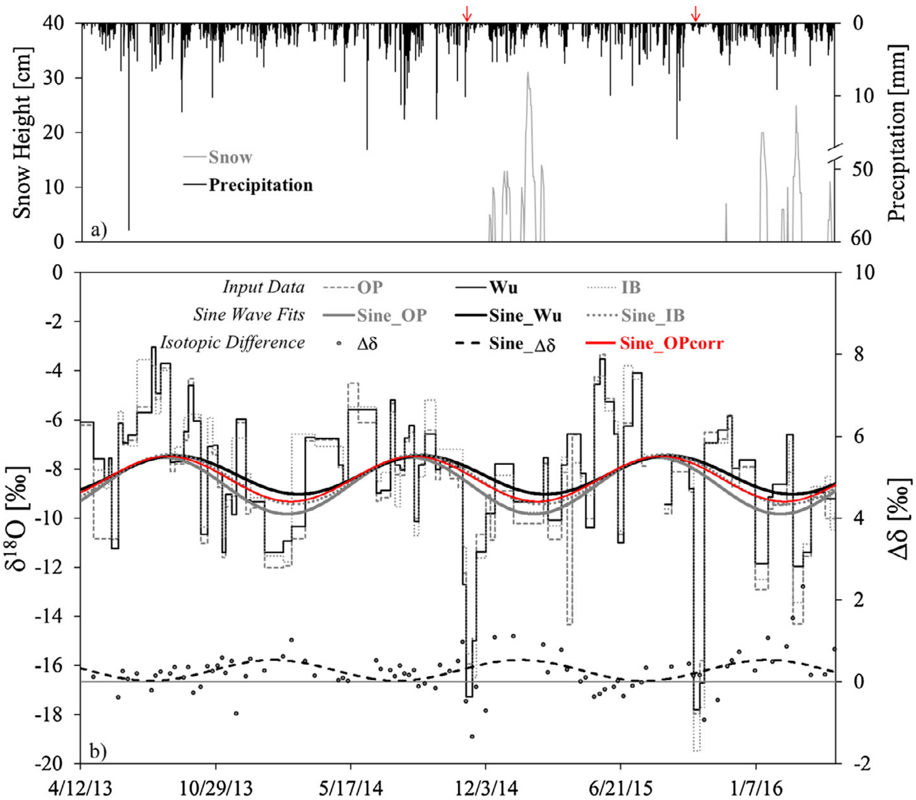

Fig. 6. (a) Precipitation and snowfall data for the Wüstebach catchment. Red arrows mark highly negative precipitation isotope values of panel (b); (b) δOP and δTF of coniferous Wüstebach site and deciduous Im Brand site together with the respective sine wave fits (Sine_x; x = OP, Wu and IB respectively). Isotopic differences of Wüstebach δTF-δOP (Δδ) were fitted by a sine wave (Sine_Δδ) and used to correct δOP data (Sine_OPcorr). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Sine wave parameters and their p-value (statistic of significance) of streamflow (Stream) and the precipitation inputs δTF_{ref}, δOP and δOP_{Sine} as well as the deciduous forest station (Im Brand). Amplitudes (Amp), phase shifts (Phase) and the Root Mean Square Error (RMSE) are given for each sine wave.

	Cosine [−]		Sine [−]		Intercept [‰]		Amp	Phase	RMSE
	Value	p-Statistic	Value	p-Statistic	Value	p-Statistic	[‰]	[rad]	[‰]
δTF_{ref}	−0.59	0.022	0.52	0.027	−8.24	~0	0.78	−0.85	2.70
δOP	−0.61	0.031	0.98	~0	−8.68	~0	1.15	−0.55	2.65
δOP_{Sine}	−0.55	0.048	0.73	0.005	−8.40	~0	0.92	−0.65	2.73
Stream	−0.08	~ 0	0.05	0.002	−8.39	~0	0.10	−1.03	0.16
Im Brand	−0.68	0.019	0.75	0.006	−8.42	~0	1.01	−0.74	2.88

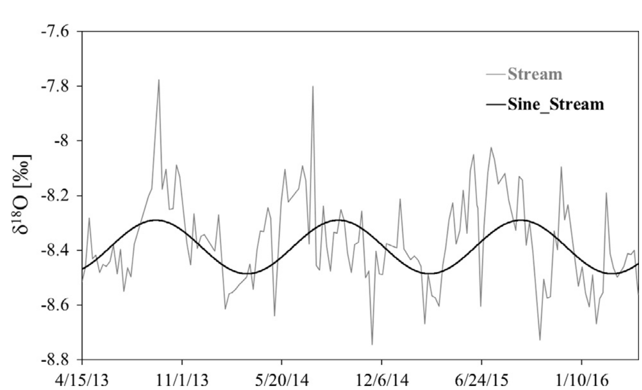

Fig. 7. Sine wave fit (Sine_Stream) of streamflow isotope data (Stream).

series into hydrological years affects the sine waves as well as F_{yw} and τ_{yw} results. For a more detailed discussion we refer to the Supplementary Material.

3.3.2. Calculations split in two hydrological years

The sine wave fit R^2 values mostly improved for δTF_{ref}, δOP, δOP_{Sine}, Δδ and the stream for the first (0.49, 0.62, 0.48, 0.17 and 0.23) and the second year (0.41, 0.36, 0.45, 0.63 and 0.50). The phase shift of the first hydrological year deviates less from the single sine wave than the phase shifts of the second hydrological year

Table 2
Optimized fraction of young water results for the simple and the complex calculation method which were calculated with δTF_{ref}, δOP and δOP_{Sine}.

		Simple	Complex
δTF_{ref}	τ_{yw} [days]	–	39
	F_{yw} [%]	12.5	12.6
δOP	τ_{yw} [days]	–	46
	F_{yw} [%]	8.5	8.8
δOP_{Sine}	τ_{yw} [days]	–	44
	F_{yw} [%]	10.7	11.0

τ_{yw}, young water threshold; F_{yw}, fraction of young water.

(Fig. 8). This indicates that the single sine wave is indeed an oversimplification of the time series behavior, especially in the second half. However, one must consider that the phase shift is sensitive to noise in the data and not as reliable as the fitted amplitudes (Kirchner 2016). Another explanation for the improved fit statistics could be a sensitivity of calculation results to the choice of the calculation time frame. However, currently we believe the second possibility to be less likely as most R^2 values improved.

For both hydrological years our correction method using δOP_{Sine} yielded results more similar to δTF_{ref}, albeit with reduced efficiency compared to the whole year calculation. In the first hydrological year δTF_{ref} resulted in 6.0% of streamflow younger than 37 days (the simple and complex method both agreed on about 6.0%), while δOP produced 5.6–5.7% and 43 days. Our correction slightly improved on this with 6.2–6.3% and 41 days. In the second hydrological year, δTF_{ref} had 13.1–14.5% for 66 days, δOP had considerably less with 7.4–8.1% for 55 days and, lastly, δOP_{Sine} resulted in 8.5–9.5% for 60 days.

F_{yw} results of the whole time series calculations lie between the results of the first and second hydrological year calculations. For example, regarding δTF_{ref} the F_{yw} for the whole time series was 12.5–12.6% which lies between results for the first and second year calculations, 6.0% and 13.1–14.5% respectively. This is a promising result, as one would expect that the whole year calculation averages results gained by sub-sets of the time series.

We looked at the overall range (min, max) of F_{yw} values of both calculation methods to evaluate the uncertainty as a result of the choice of method. In a thus defined uncertainty band, F_{yw} values for δTF and δOP_{Sine} resembled each other very closely (6–14.5% younger than 37–66 days and 6.2–11.0% younger than 41–60 days, respectively) while δOP was far off from this result with 5.6–8.8% younger than 43–55 days. Thus, F_{yw} modeling with δOP_{Sine} data revealed an uncertainty very well comparable to the uncertainty of F_{yw} derived from the original δTF time series.

Future studies should investigate the splitting up of multi-year time series into individual years, as the possibility exists that other catchments also show temporally varying tracer sine waves. We tentatively recommend using hydrological years to calculate F_{yw} based on the analyses done here, but these recommendations are contingent upon more robust analyses to be executed in the future (e.g., using a synthetic dataset as recommended by Kirchner [personal communication]). We currently recommend using hydrological years to calculate F_{yw}. Alternatively, a moving time window could be used to evaluate its temporal changes. Combined with time-variant transit time distribution estimates, this could be a valuable asset in determining time-variable catchment water transport.

3.4. Correcting open precipitation data – a way forward

We found that our method improved on previous attempts that simply shifted δOP uniformly towards enriched values. Inadequate correction of δOP will also affect chemical tracers that are altered during forest canopy passage (Adriaenssens et al., 2012; Pichon et al., 1996) or other applications than studying water movement, e.g., relating plant water to meteorological water (Brienen et al., 2013). Previous studies already developed models of isotopic change in intercepted snow (Claassen and Downey, 1995) or rainfall (Saxena, 1986). However, these methods need hard-to-obtain variables such as the δ-value of atmospheric vapor or isotopic fractionation factors. In comparison to this, the method presented here only needs relatively simple measurements, relying on the measurement of δTF. One could argue that if δTF needs to be measured it might as well be directly used. However, it might be feasible to complement already existing δOP time series with much shorter δTF time series revealing the basic enrichment Δδ pattern for the respective catchment.

We recommend verifying the existence of a seasonal Δδ pattern in other temperate forests to further develop methods for the substitution of δTF measurements with δOP correction functions. We expect such a pattern to vary from year to year. To nevertheless use it without measuring δTF would consequently require relating it to other parameters, e.g., standard meteorological variables or canopy parameters. Furthermore, future studies need to address the improvement of the new estimate (F_{yw} from δOP_{Sine}) with respect to the reference (F_{yw} from δTF) including the respective uncertainties associated with e.g., input data and parameter estimates.

Presently, we recommend setting up TF monitoring locations at different catchments under e.g., different climate conditions and forest types (e.g. deciduous trees) to evaluate for which conditions the sine wave correction method is suitable. Currently, we assume humid, snow-influenced catchments to have the highest likelihood of showing similar patterns as in the present study and base this conjecture on similarities of our data to the study of Claassen and Downey (1995).

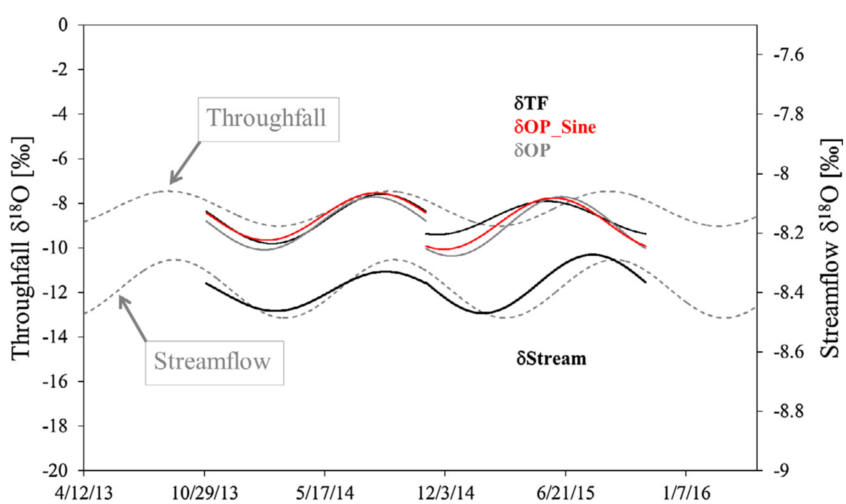

Fig. 8. Sine waves of throughfall and streamflow (grey, dashed lines). Compared to this the sine waves calculated for the two hydrological years for δTF, δOP_{Sine} and δOP, as well as the streamflow sine waves.

4. Conclusions

Previous studies showed that canopy-induced changes of the isotopic tracer signal in precipitation affect hydrograph separation and the estimation of the transit time distribution. This finding demands either the measurement of δTF or the development of adequate correction methods for open precipitation. In this study, we investigated a three year long time series of weekly δOP and δTF measurements and found a seasonal behavior in the difference between δOP and δTF (Δδ). The occurrence of the largest differences during winter months can likely be explained by the longer exposure of snow to environmental impacts (before melting) and the increased isotopic fractionation during cooler temperatures. The observed pattern in Δδ was fitted by a sine wave, which was then applied as a correction function for δOP. As a first benchmark test, the fraction of young water in streamflow (F_{yw}) was calculated with δTF_{ref} as a reference and compared to δOP and δOP corrected by the fitted Δδ-sine wave (δOP_{Sine}). We found that δOP_{Sine} was able to provide results more similar to δTF_{ref}, while δOP produced the largest deviations from the reference. However, further studies are needed to test the applicability of the correction method on other catchments, to test whether F_{yw} is an appropriate quality measure and to include uncertainty metrics. Our study stresses that canopy interception-induced changes of δOP are relevant in isotope-based transit time studies. Therefore, it is essential to consider these variations in hydrological studies while a constant correction term for δOP is not appropriate. Currently, we highly recommend measuring TF in forested catchments to further our knowledge about deriving correction functions for δOP in different catchments and their dependence on e.g., meteorological variables.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jhydrol.2017.10.003.

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