Time-variability of the fraction of young water in a small headwater catchment

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Abstract. The time precipitation needs to travel through a catchment to its outlet is an important descriptor of a catchment’s susceptibility to pollutant contamination, nutrient loss and hydrological functioning. The fast component of total water flow can be estimated by the fraction of young water (Fyw) which is the percentage of streamflow younger than three months. Fyw is calculated by comparing the amplitudes of sine waves fitted to seasonal precipitation and streamflow tracer signals. This is usually done for the complete tracer time series available neglecting annual differences in the amplitudes of longer time series. Considering inter-annual amplitude differences, we here employed a moving time window of one-year length in weekly time steps over a 4.5-years δ¹⁸O tracer time series to calculate 189 Fyw results. The results were then tested against the following null hypotheses, defining 2% difference in Fyw as significant based on results of previous studies: (1) Fyw does not deviate more than ±2% from the mean of all Fyw results indicating long-term invariance. Larger deviations would indicate either flow path changes or a change in the relative contribution of different flow paths; (2) for any four-week window Fyw does not change more than ±2% indicating short-term invariance. Larger deviations would indicate a high sensitivity of Fyw to a 1-4 weeks shift in the start of a one-year sampling campaign; (3) for a given calendar month Fyw does not change more than ±2% indicating seasonal invariance of Fyw. In our study, all three null hypotheses were rejected. Thus, the Fyw results were time-variable, showed a high variability in the chosen sampling time and had no pronounced seasonality. Based on high short-term variability of Fyw when the mean adjusted R² was below 0.2 we recommend that a low R² should be regarded as indicating potentially highly uncertain Fyw results. Furthermore, while investigated individual meteorological factors could not sufficiently explain variations of Fyw, the runoff coefficient showed a moderate negative correlation of r = -0.54 with Fyw.

This indicated that when annual runoff exceeded precipitation the catchment received the water deficit from storage which is old water causing a decrease in Fyw. The results of this study suggest that care must be taken when comparing Fyw of catchments that were based on different calculation time periods.

1 Introduction

Precipitation water uses slow and fast flow paths on its way through a catchment to the outlet where it becomes streamwater [Tsuboyama et al., 1994]. Slow flow paths are for example the saturated and unsaturated flow through the soil matrix [Gannon 30...
et al., 2017] while fast flow paths include preferential flow [Wiekenkamp et al., 2016a] and overland flow [Miyata et al., 2009]. The distribution of slow and fast flow paths depends on a catchment’s spatiotemporal characteristics [Stockinger et al., 2014; Tetzlaff et al., 2009a; Tetzlaff et al., 2009b]. Knowledge of this distribution helps in assessing the risk of streamflow contamination with pollutants or nutrient loss since nutrients and pollutants are transported through the soil by hydrological pathways [Bourgault et al., 2017; Gottselig et al., 2014].

The stable isotopes of water (δ18O and δ2H) are widely applied in the study of flow paths and transit times of precipitation through a catchment [McGuire and McDonnell, 2006]. One method that utilizes the stable isotopes of water for investigating fast flow paths is the fraction of young water (Fyw). Developed by Kirchner [2016a], Fyw estimates the streamflow fraction that is younger than three months since entering the catchment as meteoric water. It does so by comparing the amplitudes of sine waves fitted to the seasonally-varying isotope tracer signal in precipitation and streamflow. The seasonally-varying isotope signal in precipitation is caused by different evaporation/condensation temperatures, vapor source areas and evaporation amounts of falling rain droplets during warmer and colder seasons, leading on average to higher δ18O values in summer and lower ones in winter months [Dansgaard, 1964]. As rainfall passes through a catchment to reach the outlet, this signal is attenuated and shifted in time, leading to a much smoother but still seasonally-varying isotope signal in streamflow. The ratio of the fitted streamflow sine wave’s amplitude $A_S$ divided by the fitted precipitation sine wave’s amplitude $A_P$ equals the percentage of water in streamflow younger than three months. Kirchner [2016a,b] showed the robustness of Fyw against spatial catchment heterogeneities (aggregation bias error) where previous methods of transit time estimation by sine wave fitting produced highly uncertain results.

Catchment influences on Fyw were, e.g., investigated globally by Jasechko et al. [2016]. They calculated Fyw for 254 catchments and concluded that one third of global streamflow consists of water younger than three months with catchments in steeper terrains having smaller contributions of young water to their runoff. Wilasz et al. [2017] did not use sine waves to estimate Fyw but coupled a rainfall generator with rainfall-runoff and time-varying transit time models to determine the young water fraction. They found an increase of annual rainfall amounts of 1 mm/d led to an increase of 3-4% in the modeled Fyw. It can be assumed that with changing environmental conditions (e.g. in terms of land-use, climate, and urbanization), Fyw will also change for a given catchment. For example, von Freyberg et al. [2018] found a positive correlation between Fyw and high-intensity precipitation events. This could lead to a long-term increase in Fyw since the precipitation intensity is expected to increase with global warming [Pendergrass and Hartmann, 2014].

Contrary to catchment characteristics influencing Fyw, the conditions and conceptualizations of the Fyw calculation also influenced results in past studies. The effect of varying sampling frequencies of tracer data was investigated by Stockinger et al. [2016]. A higher sampling frequency led to higher Fyw highlighting the sensitivity of Fyw to the temporal resolution of the available tracer data. Lutz et al. [2018] investigated 24 catchments in Germany and used 10,000 Monte Carlo simulations with
random errors in the isotope data of precipitation and streamflow to derive the 95% confidence intervals of Fyw. Their confidence intervals were narrow, indicating a robustness of Fyw against random errors in input data. The study of von Freyberg et al. [2018] focused on three influences on Fyw: (a) spatially interpolating precipitation isotopes, (b) including snow pack and (c) weighing streamflow in fitting sine waves. They found that weighing streamflow led to significant changes in Fyw while the other factors had a negligible effect.

Past studies fitted one sine wave for the complete time series length available, varying from less than a year to several decades [Ogrinc et al., 2008; Song et al., 2017; von Freyberg et al., 2018]. However, it remains to be tested how sensitive the Fyw method is towards the timing and the length of the available data. Therefore, the present study investigated the temporal variability of Fyw. We used a one-year time window which was moved in 7-days steps to calculate 189 Fyw estimates over a 4.5-year time series of isotope data to test the following null hypotheses:

1. Fyw estimates do not change over time (time-invariance)
2. Short-term changes in the start of a tracer sampling campaign do not influence the Fyw estimate (sampling-invariance)
3. Fyw estimates are similar for a given calendar month of different years (seasonal-invariance)

The three hypotheses were tested against rules of acceptance that were based on whether differences in Fyw exceeded a threshold value of ±2%. Should a null hypothesis be rejected, hydrometric and meteorological data will be used to investigate possible influences on time-variable Fyw results.

2 Site & Methods

2.1 Study site

The Wüstebach headwater catchment (38.5 ha) is located in the Eifel National Park (Germany, Figure 1). It is also part of the Lower Rhine/Eifel Observatory of the Terrestrial Environmental Observatories (TERENO) network [Bogena et al., 2018]. The mean annual precipitation amounts to 1107 mm (1961 – 1990) with a mean annual temperature of 7°C [Zacharias et al., 2011]. 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 gleysois, histosols and planosols are found in the riparian zone. The catchment is mostly covered with Norway spruce (Picea abies) and Sitka spruce (Picea sitchensis) [Etmann, 2009]. 8 ha (~21%) of the forest were clear-cut in August/September 2013 [Wiekenkamp et al., 2016b].

2.2 Data preparation

We used hourly hydrometric and weekly δ18O isotope data of precipitation (composite sample) and streamflow (grab sample) from October 2012 to June 2017. Precipitation depths were measured hourly in 0.1 mm increments for rainfall and daily in 1...
cm increments for snowfall at the meteorological station Monschau-Kalterherberg of the German Weather Service (Deutscher Wetterdienst DWD station 3339, 535 m asl), located 9 km northwest of the catchment. Runoff was measured at the outlet by a V-notch weir for lower and a Parshall flume for higher runoff depths in 10-minute intervals. We collected throughfall samples for isotopic analysis as the Wüstebach catchment is forested and canopy-passage of precipitation influences Fyw [Stockinger et al., 2017]. The samples were collected with six RS200 samplers (UMS GmbH, Germany) with a distance of 2 m to each other and to trees. The samplers consisted of a 50 cm long, 20 cm diameter plastic pipe which was buried in the ground. On top of it a 100 cm long plastic pipe with the same diameter was installed. An HDPE sample bottle (max. volume of 5000 ml) was placed inside the buried pipe and connected with plastic tubing to a funnel on top of the 100 cm long pipe. The funnel had a collecting area of 314 cm² and was protected by a wire mesh against foliage and a table tennis ball in the funnel served as an additional evaporation barrier. Tests of the system showed the reliability in protecting the collected water from evaporation and in consequence isotopic fractionation for several weeks [Stockinger et al., 2015]. Two samplers of the same design were placed in a clearing of the Wüstebach catchment to sample open precipitation, i.e., precipitation that has not passed through the spruce canopy. Streamflow samples for isotopic analysis were collected weekly as grab samples in HDPE bottles at the outlet of the catchment.

Isotopic analysis was carried out using laser-based cavity ringdown spectrometers (models L2120-i and L2130-i, Picarro Inc., USA). 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 [Brand et al., 2014]. The precision of the analytical system was ≤ 0.1 ‰ for δ¹⁸O.

We calculated weekly volume-weighted means of δ¹⁸O for throughfall and open precipitation, which were further weighted according to the respective land-use percentage of spruce forest (79%) and clear-cut (21%) areas to generate a time series of precipitation δ¹⁸O for the whole catchment. The derived precipitation isotope time series was then used together with the weekly streamwater grab samples to calculate Fyw. While streamflow never ceased and thus a time series of weekly isotope values was available for the whole time series, there were weeks of no precipitation and thus gaps in the time series. Because of this on average 43 isotope values were available for precipitation compared to 53 values for streamflow. Furthermore, we could not always sample precipitation in weekly intervals, leading to bulk samples of 2-3 weeks on occasion. In this case, we assigned the measured bulk isotope value to each week, while the measured bulk precipitation depth was proportionally assigned to each week according to the distribution of hourly precipitation measured at the meteorological station Kalterherberg.

Additionally, for further data analyses we used air temperature and relative humidity measured in 10-minute intervals at the TERENO meteorological station Schleiden-Schöneseifen (Meteomedia station, 572 m asl), located 3 km northeast of the catchment.


2.3 Fraction of young water

The three hypotheses were tested by first calculating 189 Fyw results using a moving time window approach and then testing their characteristics against predefined rules. Fyw is calculated by fitting a sine wave to both the seasonally-varying precipitation and streamflow isotope signals, respectively. We used the multiple regression algorithm IRLS (iteratively reweighted least squares, available in the software R) to minimize the influence of outliers during sine wave fitting:

\[ C_P(t) = a_P \cos(2\pi ft) + b_P \sin(2\pi ft) + k_P, \]
\[ C_S(t) = a_S \cos(2\pi ft) + b_S \sin(2\pi ft) + k_S \]

(1)

with \( C_P(t) \) and \( C_S(t) \) the simulated precipitation and streamflow isotope values of time \( t \), \( a \) and \( b \) regression coefficients, and \( k \) and \( f \) the vertical shift and frequency of the sine wave. The difference of \( C_P(t) \) and \( C_S(t) \) to the measured isotope time series in precipitation and streamflow is minimized to fit the parameters \( a \), \( b \) and \( k \), while the frequency \( f \) of the sine wave is known due to its annual character (i.e., if \( C_P(t) \) and \( C_S(t) \) are calculated in hourly time steps then the frequency \( f \) is \( 1/8766; \) 24 hours multiplied by 365.25 days). The goodness-of-fit of the sine waves are expressed as the adjusted coefficient of determination \( R^2 \). If not otherwise stated we will use the mean of the streamflow and precipitation adjusted \( R^2 \) values further on, as both sine waves are needed to estimate the fraction of young water. After fitting these multiple regression equations, the amplitudes \( A_P \) and \( A_S \) and Fyw can be calculated as:

\[ A_P = \sqrt{a_P^2 + b_P^2}, \quad A_S = \sqrt{a_S^2 + b_S^2}, \]
\[ F_{fyw} = \frac{A_S}{A_P} \]

(2)

We used a moving one-year time window which was moved in 7-days steps to calculate 189 Fyw estimates over the 4.5-year time series. A minimum time window length of one year was chosen to fully capture the annual isotope signal.

Shifting the calculation window in 7-days steps resulted in a time series of varying Fyw estimates. Of course, the Fyw estimates cannot be considered independent from each other precluding the use of regression analysis to derive predictor variables (e.g., temperature, relative humidity) for the independent variable (Fyw). However, we used regression analysis to describe the average meteorological conditions during each Fyw time window. The thus derived “predictor” variables may have influenced Fyw and could be investigated in future studies that use Fyw estimates independent of each other.

Apart from the 189 sine waves, we also calculated Fyw for the whole time series with one sine wave and compared the timing of peaks and the individual amplitudes of the moving time-window approach to it.
2.4 Hypotheses testing

We defined 2% difference in Fyw as significant (absolute percentage points and not a relative change) as *Lutz et al.* [2018] estimated the standard deviation of Fyw due to the uncertainty in regression coefficients with a mean of 0.02. Furthermore, prior studies in the Wüstebach catchment identified changes of Fyw between 2-4% as significant [*Stockinger et al.*, 2016; *Stockinger et al.*, 2017].

Based on this definition of a significant change in Fyw, three hypotheses were tested according to the following rules of acceptance:

1) **Fyw estimates do not change over time (time-invariance)**

   This hypothesis is accepted if more than 90% of Fyw values are within ±2% of the mean value of all Fyw results. We chose a minimum percentage of 90% to ensure that the long-term time-invariance is captured. Larger changes of Fyw over time would indicate either flow path changes or a change in the relative contribution of different flow paths. In case of the exceedance of ±2% change we investigated correlations of Fyw with hydrometric and meteorological variables.

2) **Short-term changes in the start of a tracer sampling campaign do not influence Fyw estimate (sampling-invariance)**

   This hypothesis is accepted if four consecutive Fyw results (i.e., four weekly shifts of the one-year time window) do not differ more than ±2%. We thus investigated 186 four-week time windows of the in total 189 Fyw estimates. The short time span of four weeks ensures that the influence of possible long-term changes in catchment flow paths are not captured and only the influence of the starting and end time of sampling one year of isotope data is investigated. In the case that Fyw shows stronger variations, the sampling time will likely have influenced Fyw results. Patterns to help identify such situations beforehand are then searched by analyzing the time of occurrence of these situations.

3) **Fyw estimates are similar for a given calendar month of different years (seasonal-invariance)**

   This hypothesis is accepted if Fyw for the individual months does not differ more than ±2% within each month (for example, for each January Fyw lies between 7 – 9%). We would conclude that the catchment reacts similar for a given season if the hypothesis is accepted. If it is accepted and the Fyw estimates vary from month to month it would indicate a seasonal change in the dominance of certain flow paths. However, it is also possible that the hypothesis is accepted if Fyw is constant for all 189 results, as only the intra-month variance matters with this hypothesis. Then the flow paths would not change throughout the year. Contrary to the acceptance of the hypothesis, rejecting it for most months would indicate that there are no distinct seasonal patterns imprinted on Fyw.

An example of a theoretical Fyw time series is given in Figure 2. Despite it having a time-variant young water fraction, all three hypotheses are accepted. On a long term basis, the young water fraction does not deviate significantly from its overall mean value (time-invariance), choosing to start a one-year long sampling camping on a specific date or e.g., two weeks later...
would not significantly alter the result (sampling-invariance) and results show a seasonal behavior that is stable over longer time frames (seasonal-invariance). Therefore, these results would represent a runoff with seasonally-varying fraction of young water from a catchment with stable environmental conditions and water transport properties, and low sampling uncertainties.

For clarity we want to highlight that in the following presentation of results each data point was placed in the midpoint of the year it represents. That is, a data point located at any date represents the value for the six months before and six months after this date. For example, a Fyw result of 0.2 on 6th August 2013 means that between 5th February 2013 to 4th February 2014 on average 20% of runoff consisted of water younger than three months. The same logic applies to adjusted $R^2$ values, amplitudes, phase shifts and hydrometeorological data. The hydrometeorological data was calculated as mean values for the 189 individual calculation years to facilitate comparison to the Fyw results that are averages valid for the respective calculation time frame.

3 Results

3.1 Isotopic and hydrometric data

Precipitation isotope ratios ranged from -3.04 to -17.80‰, spanning a range of 14.76‰ in $\delta^{18}O$ values. In comparison, streamflow values ranged from -7.78 to -8.74‰ with a range of 0.96‰ or only 1/15th of precipitation values. The maximum and minimum air temperatures were 27.0 and -7.4 °C, respectively, with a mean value of 7.6 °C. Relative humidity ranged from 96.8 to 32.3% with a mean of 82.2%. All the sampling years except winter season 2013/14 experienced a build-up of snow pack with a mean height of 15 cm. The absence of snow in 2013/14 correlated with on average higher temperatures (3.5 times the average temperature of the other years) and lower relative humidity (5% lower average relative humidity compared to the other years).

3.2 Fraction of young water

The single sine waves for the whole study period fitted the 156 precipitation and 195 streamflow $\delta^{18}O$ values with adjusted $R^2$ of 0.08 and 0.2, respectively. The precipitation amplitude $AP = 0.72‰$ and the streamflow amplitude $AS = 0.08‰$ resulted in a Fyw of 10.8%.

The 189 individually fitted sine waves showed strong variations in terms of amplitudes and phase shifts leading to distinct deviations from the sine wave fitted to the whole time series (Figure 3). Precipitation amplitudes ranged between 0.26 to 2.60‰ with a mean value of 1.23‰ while streamflow amplitudes ranged between 0.03 to 0.19‰ with a mean value of 0.10‰. The mean of all streamflow amplitudes was closer to the single sine wave amplitude (0.10‰ vs. 0.08‰) than the precipitation amplitudes (1.23‰ vs. 0.72‰). Thus, if we would use the averages of the individual sine wave amplitudes to calculate Fyw, the result would be 9.3% instead of 10.8% of the single sine wave. This is less than the 2% difference in Fyw defined as a threshold value for significant differences by this study. The overall pattern of the individual peaks was similar to the single
sine wave peaks, except for a period between June to October 2015 when a distinct double-peak appeared in the precipitation data. The individual sine waves also followed the general pattern of enriched isotopic values during summer months and depleted values in winter.

The mean of adjusted $R^2$ of the sine wave fits of precipitation and streamflow showed a marked decrease during July 2014 to October 2015 with values falling well below 0.2 and individual sine wave fits of throughfall even had negative adjusted $R^2$ (Figure 4a). Approximately at the same time the Fyw results started to show more erratic jumps (mean and maximum change of Fyw between consecutive one-year windows: 1.6% and 10.7%). Contrary to this, during periods of higher adjusted $R^2$ the change in Fyw was more modest (mean and maximum change of Fyw between consecutive one-year windows: 0.6% and 4.2%). We compared the period of low adjusted $R^2$ to the amplitudes, phase shifts and vertical shifts of the individual sine waves to find possible modeling influences on the drop and subsequent recovery of adjusted $R^2$ but only show results for amplitudes, as the other parameters had no correlation (Figure 4b). In unison with adjusted $R^2$ the mean amplitude drops below approximately 0.5‰ and then recovers again. We found that adjusted $R^2$ was strongly correlated with the mean amplitude with an $R^2$ of 0.87 (Figure 5). Sine wave adjusted $R^2$ values below 0.15 cluster apart from most other data points.

All 189 Fyw results were not normally-distributed but positively skewed (Figure 6). Around 30% of results indicated 5% of young streamwater, followed by still a large relative frequency of up to 10% Fyw. Few values are higher than 16% Fyw with a possible outlier at 32%. Leaving out the period of low adjusted $R^2$ values does not change the skewness of the histogram. However, values of Fyw larger than 16% disappeared in favor of 5% Fyw that shifted from 30% to 40% relative frequency.

### 3.3 Hypothesis 1: Time-invariance

The mean value of all Fyw results was 9.3%. Consequently, 90% of all Fyw results must lie within 7.3 to 11.3% to accept hypothesis 1. Out of the 189 Fyw results 63, i.e. 33%, were within those boundaries (Figure 7a). However, it could be possible that the period between July 2014 and October 2015 with low adjusted $R^2$ values and erratic Fyw behavior significantly influenced the rejection of the hypothesis. Therefore, in a second step we excluded this period, calculated the mean for those values and evaluated Fyw results again (Figure 7b). The new mean Fyw was 7.5% with 53% of results found between 5.5 to 9.5%. Again, there was no indication that hypothesis 1 could be accepted and it was ultimately rejected. We then investigated the alternative hypothesis that Fyw varies in time and compared it to hydrometric and meteorological measurements (Figure 8).

Neither temperature nor relative humidity were correlated with Fyw (not shown). While throughfall volume, runoff volume and snow height were also not correlated (Figure 8a-c) the runoff coefficient ($Q/P$) was negatively correlated (Figure 8d). Leaving out again the period from July 2014 to October 2015 did not alter these correlations.
3.4 Hypothesis 2: Sampling-invariance

Here we tested if short-term changes in the start of a one-year sampling campaign could significantly influence Fyw. The hypothesis is accepted if during any consecutive four weeks Fyw did not differ more than ±2%. On multiple occasions this rule was violated for the full data set, as well as for the reduced one (discounting the low adjusted $R^2$ period), so we also rejected hypothesis 2 (Figure 7). Thus, the start time of a one-year long sampling campaign could significantly influence Fyw. The periods when hypothesis 2 was violated were neither equally spaced in time (Figure 7) nor did they show significant correlations to hydrometric (Figure 8) or meteorological (not shown) variables. The only systematic behavior observable was that many outlier values in the correlation between the runoff coefficient and Fyw were part of these periods (Figure 8d).

3.5 Hypothesis 3: Seasonal-invariance

To detect a possible seasonality of Fyw we grouped together all Fyw results from a specific calendar month starting with January and ending with December (Figure 9). In none of the months was the difference in Fyw below ±2%. When leaving out the period with low adjusted $R^2$, only June and July stayed within ±2% while all other months still showed higher variations. Thus, we also rejected hypothesis 3 as our results did not indicate pronounced seasonality. Nonetheless, a trend of declining Fyw from January to August was visible.

4 Discussion

Judging by the isotope data, we generally expect that groundwater is recharged locally from precipitation as the long-term, volume-weighed $\delta^{18}O$ of precipitation with -8.53‰ was close to the quasi-constant $\delta^{18}O$ of groundwater with a 5-year mean of -8.43‰ and a standard deviation of 0.17‰. Furthermore, streamflow was substantially comprised of groundwater as the volume-weighed $\delta^{18}O$ of runoff was -8.40%, closely resembling groundwater. The study by Weigand et al. [2017] came to the same conclusion using nitrate and DOC in the Wüstebach catchment.

4.1 Sine wave fits

The general shape of the 189 precipitation sine waves compared well to the general shape of the 189 streamflow sine waves (Figure 3). Features of the enveloping curves can be found in both precipitation and streamflow, e.g., the shape of the positive and negative peaks occurring around September 2014 and 2016 and February 2013 and 2014, respectively. This indicated that throughout the 4.5-year time series the characteristic of the precipitation $\delta^{18}O$ signal was for the most part consistently and quickly transferred to the streamflow $\delta^{18}O$ signal within a year. No isotope information beyond a year could have influenced the general shape of the 189 precipitation and streamflow sine waves, as each sine wave was calculated with one year of isotope data only. Thus, considering the general hydrological observations obtained from the isotope data discussed above: a certain percentage of precipitation became groundwater while another percentage that might or might not be Fyw quickly
generated runoff, conserving the precipitation $\delta^{18}O$ signal in streamflow and resulting in the similar general shapes of the 189 sine wave pairs.

A fast transmission of precipitation to streamflow was also found by Jasechko et al. [2016], and the fact that a part of precipitation quickly becomes streamflow is already inherent in Fyw and nothing new. The new insight of this study is the unexpected close resemblance of the 189 sine waves for precipitation and streamflow although the groundwater influence seems to have dominated in the Wüstebach. The simultaneous strong attenuation of the $\delta^{18}O$ streamflow signal while at the same time retaining much of the precipitation $\delta^{18}O$ signal characteristics can be explained by mixing with a quasi-constant $\delta^{18}O$ source, e.g., with groundwater. This would not alter the pattern but only attenuate the signal. Thus, the 189 sine waves gave a strong indication that streamflow in the Wüstebach consisted of precipitation input and groundwater with no additional, unaccounted sources of runoff such as subsurface flows from outside the catchment boundaries. This supports a previous study that closed the water-balance for the Wüstebach catchment using only precipitation, evapotranspiration and runoff data [Graf et al., 2014].

The double-peak in precipitation of autumn 2015 was not found in streamflow (Figure 3). It disturbed the impression of the 189 sine waves forming a single sine wave with a negative peak around this period in precipitation, while the impression of a negative peak existed for streamflow. The double-peak coincided with the lowest runoff coefficients and was the only time the runoff coefficient fell far below 1 (Figure 8d). A value below 1 indicates that more precipitation entered the catchment as was discharged as the runoff coefficient is runoff divided by precipitation. Thus, the catchment storage increased, being a possible mechanism of buffering the double-peak signal in precipitation and not releasing it to streamflow. The double-peak cannot be captured by using a single sine wave fit which averaged the timing of both peaks in our case.

4.2 Fraction of young water

The fact that Fyw calculated with the average amplitudes of 189 precipitation and streamflow sine waves was similar to Fyw calculated with a single sine wave (9.3% vs. 10.8%) indicated that the single sine wave averaged the behavior of the 189 ones. Thus, if a study would be interested in the overall behavior of a multi-year time series a single sine wave fit would seem sufficient. However, this statement is only true if all Fyw results are used. Care must be taken when considering the period of low adjusted $R^2$ values: if this period is left out, the average Fyw of the remaining sine waves reduced from 9.3% to 7.5%. This new value is more than 2% smaller than 10.8% obtained by the single sine wave. Thus, the single sine wave would give a misleading result if later studies would show that Fyw is unreliable below a certain adjusted $R^2$ threshold. Independent of the single sine wave averaging the 189 individual results or not, hypothesis 1 was rejected meaning that Fyw varied significantly within this multi-year time series (Figure 6). Therefore, previously only an average value of Fyw was obtained for a given time series if a single sine wave was used. No detailed knowledge about the possible variability of this value was available. Using a moving time window to calculate a host of Fyw values ensures that the entire range of possible Fyw estimates is considered with an average estimate and most importantly its uncertainty.
The average adjusted R² of precipitation and streamflow sine wave fits was mostly above 0.2; however, with a period of adjusted R² values below 0.2 apparent (Figure 4). During this period Fyw started to erratically vary between calculation years compared to relatively subtle changes in Fyw before and after it. At the same time, Fyw markedly increased and exceeded 16% young water in streamflow on several occasions which is a value not reached outside this period (Figure 6). However, most of the isotope data between shifts were the same as the calculation years were only shifted by one week. Still, during the low adjusted R² period Fyw occasionally fluctuated in the order of 10% (percentage point increase, not relative increase) between one-week shifts. From a hydrological standpoint it is difficult to imagine a short-term change in flow paths of this magnitude for annual averages, even more so when often Fyw quickly recovered to its original value that it had before the fluctuation. Given that the Fyw calculation is based on comparing the amplitudes of precipitation and streamflow and a low adjusted R² indicates a weak fit to a sine wave shape, we assumed that the Fyw calculation method reached its limit below an average adjusted R² = 0.2. It became highly sensitive to a small change in input data and thus highly uncertain. Additional investigations on the sensitivity of Fyw to the goodness-of-fit (not necessarily only measured with adjusted R²) are subject to future studies. Such studies should consider that adjusted R² was highly correlated to the mean amplitudes (Figure 5), raising the question if a curve fit with adjusted R² = 0.6 is objectively better than a fit with adjusted R² = 0.3 when the underlying isotope data have completely different amplitudes. A decrease in the goodness-of-fit of the sine wave when amplitudes are low was also found by Lutz et al. [2018].

4.3 Hypothesis 1 – Fyw is time-variant

Hypothesis 1 was rejected because the Fyw varied in the long-term. Even ignoring the low adjusted R² period those variations led to significantly different Fyw results (Figure 7). For example, in December 2013 Fyw was 5.8% while two months later it increased to 9.6%, almost doubling. From summer 2016 to the end of the time series Fyw even tripled from 5.8% to 14.7%. These differences in Fyw results complicate catchment comparisons as the result does not only depend on catchment characteristics but also on when isotope data was collected. We recommend using a moving one-year time window to get an idea about the possible variability of Fyw estimates in investigated catchments instead of relying on a single value in catchment comparison studies. As far as we can tell, the recent Fyw catchment comparison study of Lutz et al. [2018] used the same sampling period for precipitation and streamflow for all 24 investigated catchments. In contrast, the studies of Jasechko et al. [2016] and von Freyberg et al. [2018] had isotope sampling periods varying in start date and overall length for the 254 and 22 investigated catchments, respectively, potentially influencing the uncertainty for the inter-catchment comparison according to the results of our study.

In the Wüstebach catchment the baseline for Fyw was around 5% (Figure 4). Before the low adjusted R² period Fyw was around 5%, increased to about 10% for a short time and then fell back to 5%. After the low R² period Fyw also fell to about 5%, before rising in the end. Thus, during the 4.5-years Fyw never fell below the baseline of 5% and we assumed that during
any one-year period the Wüstebach catchment will have at least 5% of young water in streamflow. This lower boundary is useful in assessing pollutant risk and nutrient loss in the catchment as it defines a minimum expected load that will quickly appear in the stream if combined with precipitation volumes and chemical substance concentrations.

The variability in Fyw of this study could not be explained by most meteorological or hydrometric variables. Lutz et al. [2018] found a negative correlation between annual precipitation and Fyw. The study of 22 Swiss catchments by von Freyberg et al. [2018] found significant positive correlations between Fyw and mean monthly discharge and precipitation volumes. Fyw of this study neither correlated with precipitation nor with runoff (Figure 8a and Figure 8b). Such contradictions could be explained by the different sampling periods of all mentioned studies but also by different catchment characteristics. Additionally, the present study investigated the same catchment temporally while the other studies investigated spatially different catchments. Furthermore, Lutz et al. [2018] found complex interactions between several catchment characteristics and Fyw, possibly resulting in nonsignificant linear regressions between Fyw and individual catchment characteristics. However, the runoff coefficient Q/P was negatively correlated with Fyw (Figure 8d). Physically, this could be explained by the fact that if annual runoff exceeds annual precipitation volumes then the additional runoff volumes were provided by catchment storage. This increased the percentage of old water in streamflow and decreased the Fyw since catchment storage consists of old water [Gabrielli et al., 2018].

4.4 Hypothesis 2 & 3 – Fyw is sensitive to sampling and has no seasonal pattern

While hypothesis 1 concentrated on long-term changes, hypotheses 2 focused on short-term changes where choosing to delay a one-year sampling campaign by one to four weeks could lead to significantly different results. On several occasion Fyw differed more than ±2% within four weeks, e.g., at the end of the time series (Figure 7). This means that the choice of the sampling period has a large potential for uncertainty in the Fyw estimates for studies that can monitor the stable isotopes of water in precipitation and streamflow for only one year. The obtained Fyw could be a potential outlier, a larger value or part of the Fyw baseline. As the violation of hypothesis 2 did not correlate with any meteorological or hydrometric data it was not possible to determine the conditions under which the sampling period led to higher Fyw uncertainty, making it impossible to give recommendations for the best sampling periods. The results of this study indicate that estimating Fyw with data of a single year might not be enough in understanding catchment behavior. Quoting Kirchner et al. [2004]: “If we want to understand the full symphony of catchment hydrochemical behaviour, then we need to be able to hear every note.”. A single Fyw result is one note in the symphony of potential Fyw results slumbering in multi-year data sets.

The Fyw results did not have a consistent seasonal pattern in that, e.g., results would be larger when sampling is started in summer months and lower when it is started in winter months (Figure 9). This further complicates the choice of when to start a one-year isotope sampling campaign. No matter when such a campaign would be started, we can only expect to get one Fyw out of many possible ones for the investigated catchment. However, a slight trend of decreasing Fyw is observable from
January to August. This trend could be coincidence. Future studies should provide more evidence if Fyw calculated by one year of isotope data shows a seasonal behavior or not. We recommend calculating the Fyw time series to understand the behavior of Fyw for the investigated catchment and to be able to evaluate possible uncertainties for Fyw estimation of the respective catchment.

5 The uncertainty in Fyw when only one-year of isotope data is available was already highlighted by Stockinger et al. [2017] for the same catchment. Their study calculated Fyw for two hydrological years and had a Fyw of approximately 6% and 13%, respectively. The authors concluded that using the complete time series averages sub-sets of the time series as the Fyw for the whole time series was 12.5%, so in between 6% and 13%. However, this happened by coincidence. If the two hydrological years lay anywhere on a different location of the Fyw time series, very different Fyw could have been obtained. With knowledge from the current study, we would even consider one of the hydrological calculation years of Stockinger et al. [2017] as highly uncertain.

5 Conclusions

The fraction of young water (Fyw) is a promising new measure to estimate the fast transport of precipitation through a catchment to the stream. To calculate Fyw, sine waves are fitted to the stable isotopes of water in precipitation and streamflow and their respective amplitudes compared. This is usually done for the complete time series available, ranging from less than a year to multiple years. This study used a moving one-year window to investigate the temporal variance of Fyw for a 4.5-year long time series. We found that both in the long and short term Fyw is time-variable, while showing no clear seasonal pattern. The long-term variability has implications for catchment comparison studies when different time periods are investigated. The resulting Fyw was up to three times larger between two consecutive calculation years, i.e., a shift of the one-year time series by one week. Short-term variability indicated a potentially high sensitivity to the sampling period, where a shift of 1-4 weeks in the start of a one-year long sampling campaign significantly influenced Fyw. As no pronounced seasonality of Fyw could be derived, no recommendations can be given yet as when to best start a one-year sampling campaign of stable isotope data. If it is feasible, we recommend a multi-year time series that is investigated for time-variable Fyw using e.g., the suggested method of the present study. However, based on the goodness-of-fit for all 189 calculated sine waves and the corresponding Fyw behavior, we recommend considering that Fyw based on adjusted R² below 0.2 might be highly uncertain. The present study shows the importance of considering inter-annual fluctuations in the amplitudes of isotope tracer data and consequently of derived Fyw results in further learning about the uncertainty of Fyw and in aiding in catchment comparison studies.
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Figure 1. Map showing the Wüstebach catchment and the used monitoring stations. OP Station is the open precipitation collection site, while TF Station is the throughfall station.
Figure 2. Panel (a): Example of a theoretical Fyw time series where despite the time-variance all three null hypotheses are accepted: (1) more than 90% of Fyw values lie within ±2% of the mean of all values; (2) Fyw does not change more than ±2% over the course of four weeks; (3) Fyw for each month does not change more than ±2% within a month (panel (b)).
Figure 3. Sine waves (red lines) were fitted to (a) throughfall and (b) streamflow stable isotope data (grey line) with maximum and minimum values at each point in time (black enveloping curve). In comparison a single sine wave was fitted to the complete data set for both throughfall and streamflow (green lines).
Figure 4. Fyw results plotted against (a) adjusted $R^2$ for throughfall (TF) and runoff (Q) sine wave fits and their average (Mean) and (b) sine wave amplitudes. All values are shown at the midpoint of the respective year they are valid for.
Figure 5. Regression line between the mean adjusted R² and mean amplitudes of the 189 sine waves.
Figure 6. Histograms and cumulative distribution functions of all Fyw results (black) and of the results when the low adjusted R² period is left out (low R², grey).
Figure 7. Testing hypothesis 1 and 2. The time series of Fyw compared to the mean of all values (solid grey horizontal line) and a ±2% margin around the mean (dotted grey horizontal lines). Once all data was used (panel a) and subsequently data of the low adjusted R² period between July 2014 to October 2015 was left out (panel b). Red data points are periods where within four weeks Fyw differed more than 2%.

Figure 7. Testing hypothesis 1 and 2. The time series of Fyw compared to the mean of all values (solid grey horizontal line) and a ±2% margin around the mean (dotted grey horizontal lines). Once all data was used (panel a) and subsequently data of the low adjusted R² period between July 2014 to October 2015 was left out (panel b). Red data points are periods where within four weeks Fyw differed more than 2%.
Figure 8. Fyw plotted against hydrometric data (red and black dots): a) throughfall volumes, b) runoff volumes, c) snow height, d) the runoff coefficient. Red dots are data points where hypothesis 2 was rejected.
Figure 9. Testing hypothesis 3. Boxplot of all Fyw results of a specific month. 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.