Fractions of Different Young Water Ages are Sensitive to Discharge and Land Use – an Integrated Analysis of Water Age Metrics under Varying Hydrological Conditions for Contrasting Sub-Catchments in Central Germany

Christina F. Radtke[1], Stefanie R. Lutz[2], Christin Mueller[1], Ralf Merz[1], Rohini Kumar[3], Kay Knoeller[1]

[1] Helmholtz-Centre for Environmental Research UFZ, Department of Catchment Hydrology, Germany

[2] Copernicus Institute of Sustainable Development, Utrecht University, the Netherlands

[3] Helmholtz-Centre for Environmental Research UFZ, Department of Computational Hydrosystems, Germany

Corresponding author: Christina F. Radtke (christina.radtke@ufz.de)

Key Points:

- High-frequency water isotopic signatures can unravel water age changes during short-term hydrologically varying conditions
- Young water in stream flow is sensitive to discharge variations under changing climatic conditions
- Landscape structures affect the young water contributions to stream flow with higher Fyw for agricultural catchments

Abstract

With ongoing climate change and more frequent high flows and droughts, it becomes inevitable to understand potentially altered catchment processes under changing climatic conditions. Water age metrics such as median transit times and young water fractions are useful variables to understand the process dynamics of catchments and the release of solutes to the streams. This study, based on extensive high-frequency stable isotope data, unravels the changing contribution of different water ages to stream water in six heterogeneous catchments, located in the Harz mountains and the adjacent northern lowlands in Central Germany. Fractions of water up to 7 days old (Fyw7), comparable with water from recent precipitation events, and fractions of water up to 60 days old (Fyw60) were simulated by the tran-SAS model. As Fyw7 and Fyw60 were sensitive to discharge, an integrated analysis of high and low flows was conducted. This revealed an increasing contribution of young water for increasing discharge, with larger contributions of young water during wet spells compared to dry spells. Considering the seasons, young water fractions increased in summer and autumn, which indicates higher contributions of young water after prolonged dry conditions. Moreover, the relationship between catchment characteristics and the water age metrics revealed an increasing amount of young water with increasing agricultural area, while the amount of young water decreased with increasing grassland proportion. By combining transit time modelling with high-frequency isotopic signatures in contrasting sub-catchments in Central Germany, our study extends the understanding of hydrological processes under high and low flow conditions.

1 Introduction

With an expected increase in the frequency of heavy rainfall as well as longer dry periods due to climate change (Kundzewicz et al., 2014), it becomes more and more important to understand the hydrological processes during wet and dry spells as well as the age composition of water (Wilusz et al., 2017). Thanks to the use of tracer data such as isotopic signatures of water to unravel the water age (e.g. median transit time and fraction of young water), our understanding of hydrological processes and the contribution of different water sources and their respective water ages has been improved. Water age metrics such as median transit times and fractions of young water are widely used tools to understand the hydrological pathways of catchments of different sizes. Knowledge of hydrological pathways is an inevitable prerequisite to understand and predict water and pollutant fluxes and pollutant legacies. The composition of different water ages can be simulated by models (e.g. Hrachowitz et al., 2009; Soulsby et al., 2015; Benettin and Bertuzzo, 2018; Kuppel et al., 2018) or purely derived from tracer data (e.g. Kirchner, 2016a; Kirchner, 2016b; Jasechko et al., 2016; Lutz et al., 2018).

In studies where the water age is estimated, low-frequency tracer data in timesteps of weekly or monthly data can be used to get an impression about general hydrological processes in catchments (e.g. Lutz et al., 2018; Borriero et al., 2022). However, as shown by von Freyberg et al. (2017) and von Freyberg et al. (2018), sampling frequencies of daily and sub-daily resolutions can provide more detailed information about short-term hydrological processes such as storm runoff events. Lutz et al. (2018) investigated several catchments in the Bode watershed, in central Germany with the focus on estimating fractions of young water with monthly isotopic signatures of water to improve transit time distribution estimates. They found that mean ages of river water range between 9.6 months and 5.6 years depending on catchment characteristics. However, one limitation of the application of low-frequency (i.e. weekly or monthly) tracer data is the insufficient representation of the short-term dynamics such as high flow events and their corresponding hydrological processes (Stockinger et al., 2016, von Freyberg et al., 2018). In contrast, von Freyberg et al. (2017) and von Freyberg et al. (2018) estimated fractions of young water in several Swiss catchments in a daily to sub-daily resolution of tracer data to investigate relationships between young water fractions and catchment characteristics as well as climatic conditions such as storm runoff. Few studies have analyzed the water age in catchments with high resolution isotope data sets during hydrologically divergent periods (e.g., von Freyberg et al., 2017, von Freyberg et al., 2018). Knapp et al. (2019) showed in their analysis of new water fractions and transit time distributions at the Plynlimon experimental catchments in mid-Wales that estimates of water age metrics are affected by sampling frequency. Stream flow isotopic signatures are more damped with lower sampling frequency, which causes a strong difference between water age estimates derived from 7-hour and weekly tracer data (Knapp et al., 2019). Especially, for the analysis of water from previous precipitation events, von Freyberg et al. (2017) showed the relevance of high-resolution isotopic signatures for water age estimates. In a sampling interval of 30 minutes, stream water isotopic signatures were analyzed to estimate event water for eight storm events, which demonstrated the high variability during different storm events as well as a more precise estimation of event water with high-frequency isotope data compared with aggregated isotope data for lower sampling resolutions (von Freyberg et al., 2017). This highlights the potential of high-frequency tracer data applications to understand hydrological processes and their variability during varying climatic conditions such as high and low flows and furthermore implies that that more research is needed in this regard.

In view of ongoing and predicted climate change impacts resulting in more frequent high intensity precipitation events and associated storm runoff as well as longer dry periods, there is an urgent need to gain more information about the underlying processes and sources of water during hydrologically divergent periods. To unravel hydrological processes and their dependencies, studies focused on the relation between water age and catchment characteristics such as catchment area, soil type, elevation, land use as well as hydrological indices such as rainfall intensity and discharge (Soulsby et al., 2006; Hrachowitz et al., 2009; Tetzlaff et al., 2009; Jasechko et al., 2016; Wilusz et al., 2017; Lutz et al., 2018; von Freyberg et al., 2018a, Dimitrova-Petrova et al., 2020, Jutebring Sterte et al., 2021). Jasechko et al. (2016) analyzed young water fractions of 254 watersheds globally with regard to catchment characteristics. The analysis revealed high contributions of young water (30%) for most of the catchments with higher young water fractions for agriculturally dominated catchments. On the one hand, these studies highlight the dependency of flow paths and water sources on catchment characteristics. On the other hand, they emphasize the need to understand this interconnectivity in more detail. Most recent studies have investigated the overall relationship between the water age and catchment characteristics, but so far there are very few studies only focusing on the role of water age during varying discharge related to high and low flows (von Freyberg et al., 2017, von Freyberg et al., 2018b). To overcome the blind spot on short term hydrological dynamics of previous studies linking water age distribution based on low-frequency data to climate and landscape features, this study uses high-frequency isotope data and transit time modelling to reveal the difference of age compositions during varying flow conditions in streams, investigating six contrasting sub-catchments within the Bode watershed in Central Germany. We are particularly interested in understanding how stream water age is changing between hydrologically divergent periods such as wet and dry spells and how this is controlled by catchment characteristics. On the basis of an exceptionally extensive high-frequency water stable isotope data set provided by an elaborate isotope monitoring program, the aim of our investigation is (i) to understand how the age distribution of stream water is influenced during hydrologically divergent periods such as wet and dry spells, and (ii) to characterize the effect of catchment characteristics on stream water age during wet and dry spells. These analyses will allow us to inspect the relationship between water age distributions and landscape structures to support a better understanding of flow paths under varying hydrological conditions that occur with the projected climate change. Such understanding is of extreme relevance for the prediction of potential nutrient losses and of changed fluxes and legacies of pollutants that may harm the ecosystems.

2 Materials and Methods

2.1 Study area and data

The intensively studied Bode catchment is located in the Harz mountains and the adjacent northern lowlands in Central Germany (Wollschläger, Attinger et al. 2016, Lutz, Krieg et al. 2018). The mesoscale, lower-mountain range Bode catchment is part of the Elbe river basin and ranges between 55 and 1100 m above sea level showing a strong gradient in landscape characteristics from forested headwater catchments to intensively cultivated lowland catchments. It has a humid climate with a mean annual temperature about 9 °C and mean annual rainfall of 660 mm, ranging spatially between 450 and 1600 mm. There are several sub-catchments such as the Selke basin or the Holtemme basin where many studies with respect to water fluxes and water quality have been conducted (e.g., Wollschläger, Attinger et al. 2016; Lutz, Krieg et al. 2018; Borriero et al., 2022). In this study, we focus on six sub-catchments within the Bode watershed that differ in their size and catchment characteristics such as land use, geology or elevation (Figure 1 and Table 1). An elaborate monitoring program was conducted to provide extensive high-frequency isotope data sets. Automatic samplers specifically designed and proven to collect water samples for isotope analyses avoiding any evaporation effects (Michelsen et al., 2019) were set up at the outlets of five catchments. Aside from the stream water autosamplers, five autosamplers were set up to collect high-frequency precipitation samples. Furthermore, stream water samples at one location (Ilse) and precipitation samples at two locations (Ilse, Meisdorfer Sauerbach) were collected manually on a daily base by citizen scientists who were appointed for the monitoring program.

Topographic indices such as elevation, slope and topographic wetness index (TWI) were calculated using the Saga toolbox in QGIS version 3.18.1. Land use shares are taken from Corine Landcover 5 ha (GeoBasis-DE / BKG, 2018). Hydroclimatic indices such as annual average discharge were obtained from discharge measuring stations provided by the Landesbetrieb für Hochwasserschutz und Wasserwirtschaft (Landesbetrieb für Hochwasserschutz und Wasserwirtschaft, 2022). Annual average precipitation is obtained from measuring stations operated by the Deutsche Wetterdienst (DWD, 2021), whereas baseflow index (BFI) is calculated using the daily discharge datasets of all six catchments and the hydroEvents package (https://CRAN.R-project.org/package=hydroEvents) in R using version 4.0.5.

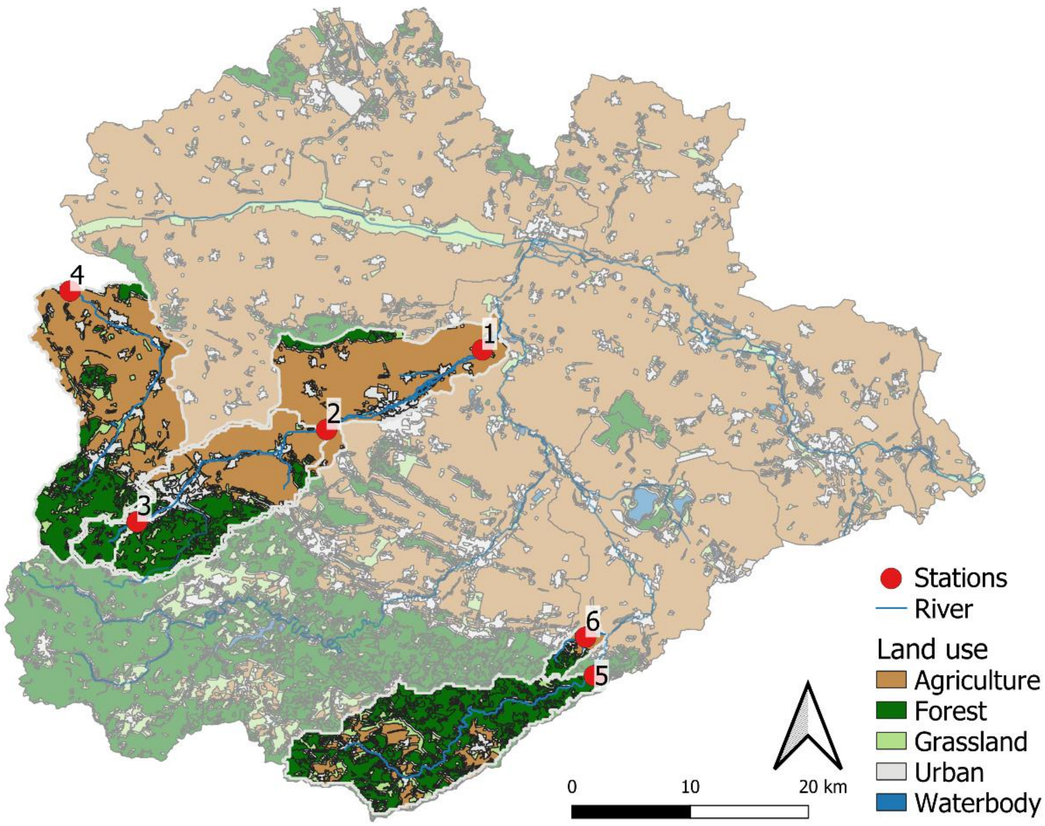


Figure 1: Selected catchments from the Harz mountains and the adjacent northern lowlands with their respective land use, where the Stations indicate the locations of both, the stream water and precipitation sampling

Table 1: Catchment characteristics with TWI as topographic wetness index and BFI as baseflow index considering time series between 2010 and 2021

Catchment characteristics	1 (Nienhagen)	2 (Mahndorf)	3 (Steinerne Renne)	4 (Ilse)	5 (Selke)	6 (Meisdorfer Sauerbach)
Area [km²]	282	142.86	13.37	194	157	11.5
Elevation [m a.s.l.]	84-863	134-863	300-863	97-1138	193-576	170-353
Forest [%]	23	25	33	22	31	36
Grassland [%]	33	37	67	40	44	15
Agriculture [%]	18	13	0	19	13	27
Urban [%]	25	24	0	19	11	22
Soil type	Chernozem, brown earth, gley soils, podzols, luvisols	Brown earth, luvisols, chernozem sub-types, podzols	Brown earth podzol with mixtures of clay	Luvisols, gley soils, podzol-brown earth, chernozem, brown earth	Brown earth, luvisols	Brown earth, luvisols, gley soils
TWI (mean)	11-28 (16)	11-27 (15)	11-20 (15)	11-24 (16)	12-23 (15)	12-23 (15)
Slope [°] (mean)	0.01-21.29 (2.9)	0.01-21.29 (4.04)	0.39-20.87 (7.95)	0.01-25.82 (2.98)	0.16-17.55 (3.77)	0.03-6.55 (2.31)
Flow path length [km]	42.66	23.09	2.07	28.68	30.12	7.37
Annual avg. discharge [mm]	102	208	529	160	128	40
BFI	0.48	0.62	0.55	0.60	0.55	0.26
Annual avg. precipitation [mm]	424	465	576	538	547	548

The sub-catchments selected for high-frequency isotopic sampling cover a wide range of climate and landscape characteristics of the Bode river basin. The largest sub-catchment is a hilly anthropogenically impacted catchment (Nienhagen catchment, 282 km^2) (Fig. 2, catchment 1), showing the highest density of river network and including lowlands with intensive agriculture (18%) and urban area (25%). The Mahndorf catchment (142.86 km^2) (Fig. 2, catchment 2) is nested within the Nienhagen catchment and shows some anthropogenic impacts, such as urban area (24%) and agricultural crop land (13%). One of the smallest sub-catchments is Steinerne Renne (13.37 km^2) (Fig. 2, catchment 3), a typical German mid-elevation mountain range headwater catchment with dominant forest (33%) and grassland (67%) cover. The catchment may be seen as a pristine head water catchment, as no agricultural fields and no urban areas are located within the catchment. With 529 mm the discharge is highest in the Steinerne Renne catchment compared to the other catchments. The Steinere Renne is part of the Mahndorf catchment. The mountainous agriculturally dominated Ilse catchment (194 km^2) (Fig. 2, catchment 4) has the highest elevation range (ranging between 97 and 1138 m) forest (22%) and grassland (40%) dominating the upper part of the catchment and a high density of agricultural area (19%) in the lowlands. Compared to the Steinerne Renne and Mahndorf catchment, the Ilse catchment shows less discharge (160 mm). With more forested (31%) and grassland (44%) area, the Selke catchment (157 km^2) (Fig. 2, catchment 5) shows less anthropogenic impacts than the Mahndorf catchment. The Selke catchment is located in the lower part of the Harz mountains, but is still hilly and mainly forested. A neighboring catchment to the Selke is the Meisdorfer Sauerbach catchment (Fig. 2, catchment 6). It is an agriculturally dominated headwater catchment in the lowlands of the Harz mountains. This catchment is the smallest (11.5 km^2) from all investigated catchments and has the lowest annual average discharge (40 mm).

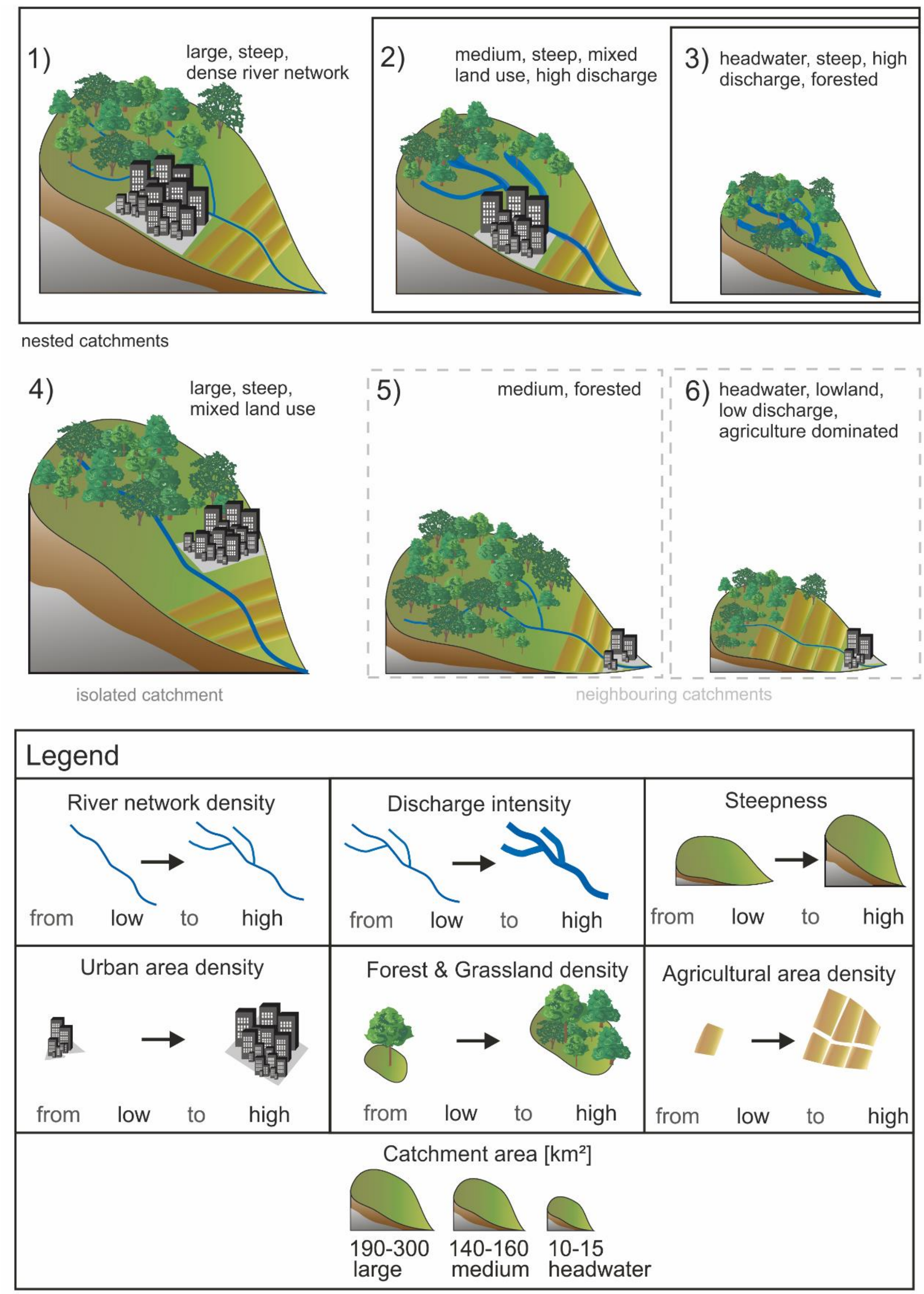


Figure 2: Illustration of all six catchments investigated, considering their most meaningful catchment characteristics

2.2 Sampling

Water samples of stream water (grab samples) and precipitation (composite samples) were collected in a monthly frequency from 2013 to 2017 for the catchments 5 and 6, and from 2013 to 2019 for the catchments 1-3. In 2020 autosamplers were set up in the catchments 1-3 and 5 to collect daily water samples of precipitation and stream water. In catchment 6 stream water was collected with an autosampler since 2020 and precipitation was collected manually. At the sampling location of catchment 4, manual samples have been taken daily from both precipitation and stream water since 2020. Event water samples were taken with the autosampler at sub-daily timesteps (4 hours to 8 hours) whenever heavy rainfall was predicted to occur following a public weather forecast. Stream water samples were taken via a pump as grab samples at specific time steps: daily samples were taken at 3 pm, and sub-daily samples were taken every 4, 6 or 8 hours, depending on the chosen program. Precipitation was sampled using a collector that switches the position of the sampling bottle at each programmed time step: 4-8 hours during a predicted precipitation event and 24 hours during daily sampling.

2.3 Laboratory analysis

Water samples were filtered through a 0.45 µm filter. A liquid isotope analyzer (Picarro L2120-I) was used for duplicate measurements of stable isotopic signatures of water. By using replicate (20x) analysis of internal standards calibrated to VSMOW and Standard Light Antarctic Precipitation (SLAP) certified reference materials, the samples were normalized to the VSMOW scale. The analytical uncertainty of $\delta^{18}O$ and $\delta^{2}H$ were ±0.1 ‰ and ±0.6 ‰ respectively. The isotopic ratios are expressed in delta notation relative to Vienna Standard Mean Ocean Water (VSMOW) for the oxygen and hydrogen isotope signatures of water:

$$\delta_{sample}[‰] = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000 \quad (1)$$

Due to higher measurement precision, the isotopic signature of $\delta^{18}O$ of water is used for the following investigations.

2.4 Data preparation

The model used in this study to estimate transit times of water requires continuous hydrological and tracer input data. For this purpose, we used hydrological outputs from a well-established Mesoscale Hydrological Model (mHM) (Samaniego et al., 2010; Kumar et al., 2013). The model was established at a 1 km spatial resolution to simulate continuous datasets of daily discharge and evapotranspiration. mHM has been thoroughly evaluated in past studies (see e.g., Zink et al., 2017; Mueller et al., 2016). Meteorological forcings such as precipitation and air temperature to drive the model were acquired from German Weather Service, DWD (DWD, 2021).

To consider the change of isotopic signatures in precipitation with elevation for all catchments investigated in this study, ordinary kriging of isotopic signatures of precipitation with elevation as external drift was conducted in R version 4.0.5. All precipitation isotope sampling locations that are located in the investigated catchments were used for kriging. The isotopic signature per day was extracted for each catchment as spatial mean of the kriged values over the catchment area for the following transit time modelling.

2.5 Transit time modelling

To model water transit times and water ages, the numerical model tran-SAS v1.0 (Benettin and Bertuzzo 2018) was set up for each catchment. By using tracer data such as isotopic signatures of water in combination with hydrological data (precipitation, evaporation and discharge), the tran-SAS model is able to simulate age metrics such as the daily median transit time as well as fractions of young water by applying storage age selection functions (SAS).
The conceptualization of each catchment is based on a single storage S(t) with a water-age balance that can be expressed as follows (Benettin and Bertuzzo, 2018):

$$S(t) = S_0 + V(t) \tag{2}$$

$$\frac{\partial S_T(T,t)}{\partial t} + \frac{\partial S_T(T,t)}{\partial T} = P(t) - Q(t) * \Omega_Q(S_T,t) - ET(t) * \Omega_{ET}(S_T,t) \tag{3}$$

$$\text{Initial condition: } S_T(T, t = 0) = S_{T_0} \tag{4}$$

$$\text{Boundary condition: } S_T(0, t) = 0 \tag{5}$$

Where S_0 is the initial storage, $V(t)$ (mm) are the storage variations, $P(t)$ is precipitation (mm/d), $Q(t)$ is discharge (mm/d) and $ET(t)$ is evapotranspiration (mm/d). $S_T(T,t)$ (mm) is the age-ranked storage with S_{T_0}(mm) as initial age-ranked storage. The cumulative SAS functions are described as $\Omega_Q(S_T, t)$ for discharge and $\Omega_{ET}(S_T, t)$ for evapotranspiration.

The SAS functions can be expressed as probability density functions with regard to the normalized age-ranked storage:

$$\omega(P_S(T,t), t) = k * (P_S(T,t))^{k-1} \tag{6}$$

$$\omega(P_S(T,t), t) = \frac{(P_S(T,t))^{\alpha-1} * (1 - P_S(T,t))^{\beta-1}}{B(\alpha,\beta)} \tag{7}$$

Where the catchment's water age preference for outflow is described by the parameters k, α and β, while $B(\alpha, \beta)$ is the two-parameter beta function. The catchment has a preference to release young water if k<1, α<1 and β<1. In case of k>1, α>1 and β>1, the catchment tends to discharge old water. No selection preference (i.e., complete water mixing) is described with k=1, α=1 and β=1. For stream water, the beta distribution SAS function (Equ. 7) was applied. Since we do not focus on the water age for evaporation and due to the lack of tracer data from evapotranspiration, we applied the time invariant power law function (Equ. 6) to evaporation fluxes for the completeness of the model. By this, we got four parameters to be evaluated using the fit of modelled vs. observed streamflow isotope data, i.e., α and β for stream water, β for evapotranspiration and the initial storage parameter S0 (Supplement Table 1). A GLUE approach was conducted to evaluate the 10% best simulations considering the Kling-Gupta-Efficiency (Gupta, Kling et al. 2009) between observed isotopic signatures in stream and simulated isotopic signatures in stream (Equ. 8).

$$KGE = 1 - \sqrt{(r-1)^2 + \left(\frac{\sigma_{sim}}{\sigma_{obs}} - 1\right)^2 + \left(\frac{\mu_{sim}}{\mu_{obs}} - 1\right)^2} \qquad (8)$$

where $\sigma_{(sim/obs)}$is the standard deviation in observations/simulations and $\mu_{(sim/obs)}$ the mean of simulation/observation, and r is the linear correlation between observations and simulations. KGE=1 indicates perfect agreement between simulations and observations. For statistical analysis of the relationship between age metrics and catchment characteristics, the mean value of the 10% best simulations was calculated for each catchment individually. In addition, the absolute bias between measured and modelled data was considered for the evaluation of the performance of the simulated isotopic signature in stream water.

2.6 Hydrologically divergent periods and statistical analysis

The discharge sensitivity was presented as a valuable tool to investigate the hydrological behavior of different catchments with each other. Von Freyberg et al. (2018) showed that Fyw were sensitive to increasing discharge, while each catchment showed different sensitivities of Fyw to discharge. Therefore, they introduced Fyw-discharge sensitivity as indicator to describe catchment specific water age dynamics. Gallart et al. (2020) developed this method further by using an exponential equation (Equ. 9) describing the relationship between Fyw and discharge:

$$Fyw(Q) = 1 - (1 - F_0) * exp(-Q * S_d) \qquad (9)$$

With F_0 as virtual Fyw for discharge (Q) being zero and S_d (unit of Q^{-1}) as a new discharge sensitivity metric (Gallart et al., 2020). Gallart et al. (2020) showed that an exponential equation is needed to ensure that Fyw cannot be above one even when discharge rises infinitely, and that for low discharges the curve approximates a linear line (Gallart et al., 2020). The discharge sensitivity presented by von Freyberg et al. (2018) was described by a linear equation. The discharge sensitivity of von Freyberg et al. (2018) equals S_d from the exponential equation of Gallart et al. (2020) as long as Fyw is lower than 1. In our study, Equ. (9) was used for two different metrics of young water to investigate the sensitivity of young water release in the catchments as a function of discharge. For comparison with other studies the fraction of water with an age up to 60 days (Fyw60), which is similar to the young water fraction with an age between 60 and 90 days according to Kirchner (2016), was obtained from the tran-SAS model as well as the fraction of water with an age up to 7 days (Fyw7) to represent recent precipitation water. We obtained the F_0 and S_d parameters with a non-linear analytic Gauss–Newton algorithm by fitting Equation 9 to Fyw7 and Fyw60 from the tran-SAS simulations, respectively. For this, the discharge was separated into 10% percentiles to cover different discharge intensities, because the daily data showed a scatter that was not be able to be represented by the Equ. 9, which plots as exponential curve.

To analyze the differing water age behavior in hydrologically divergent periods, we separated the runoff time series into dry and wet spells. We define dry spells as periods with low flow conditions, and wet spells as periods with high flow conditions. There are two common approaches in separating discharge time series. The first is a simple threshold approach categorizing periods above the threshold as wet spells, and periods below the threshold as dry spells (Lang et al., 1999, Sikorska et al., 2015). This approach has the disadvantage that parts of the same rainfall-runoff event may belong to dry spells (e.g. start of the rising limb, end or the recession), while other parts may be categorized as wet spells. For highly seasonal regimes, where seasonal variance in runoff is higher than the variance between rainfall-runoff events and no events, the threshold approach may only be able to classify according to the seasons. A second approach is a classical baseflow filtering approach, where all periods with direct flow components (i.e. rainfall-runoff events) are classified as wet spells (Merz et al., 2006, Ladson et al., 2013). This approach usually tends to lead to very short events.

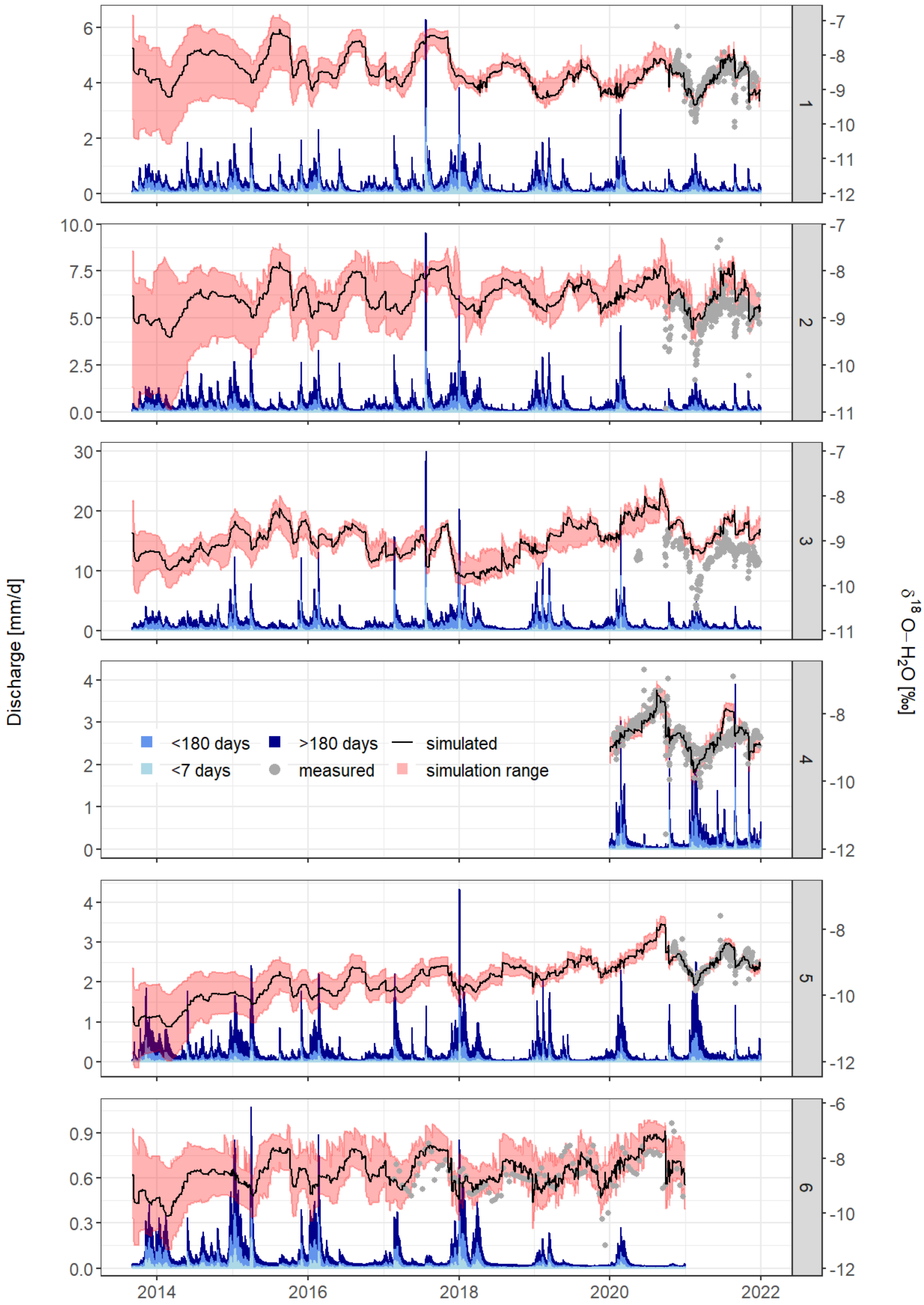
In this study we used a combination of both approaches. In a first step, single rainfall-runoff events were identified following the baseflow separation approach of Lyne and Hollick (1979) using R package hydroEvents (Ladson et al., 2013, Kaur et al., 2017, Tang et al., 2017). In a second step, all events with a peak flow in discharge higher than long-term median peak flows were categorized as wet spells, while periods with peak flows under the threshold belong to the category dry spells. By this, each catchment has an individual threshold value for wet spells corresponding to its median peak flow. No event periods were also categorized as dry spells.

This approach tends to generate longer contiguous periods of dry and wet spells, while still accounting for single rainfall-runoff events.

Wet spells and dry spells were gained from the time series 2013 to 2021, except for the catchment 4, which covers only the years 2020 to 2021, and catchment 6, where the data was available from 2013 to 2020. The relation between water age metrics (median transit time, fractions of different water ages) and catchment characteristics, such as land use share, elevation, slope and some more, of the different catchments were analyzed statistically. To understand how recent precipitation, in particular, affects the stream water age composition, the fraction of water with an age up to 7 days (Fyw7) was investigated in more detail in relation to catchment characteristics.

3 Results and Discussion

3.1 Water age modelling


Discharge [mm/d]
δ18O–H2O [‰]
<180 days
>180 days
simulated
<7 days
measured
simulation range
2014
2016
2018
2020
2022
1
2
3
4
5
6

315

Figure 3: Discharge with the different fractions of water age in light blue = water age up to 7 days, medium blue = water age up to 180 days and dark blue = water age more than 180 days for the six investigated catchments; the measured isotopic signature of discharge is shown as grey dots, while the simulated isotopic signature of discharge gained from the tran-SAS model is shown as black line; the range of simulated stream isotopic signature is shown as red shading.

In addition to measured and simulated isotope values, Fig. 3 shows the fraction of three categories of water ages: the fraction of young water up to 7 days (<7 days) highlighting water flow through fast flow paths, water up to 180 days and water older than 180 days, representing water that was stored in the catchments and/or traveled along slow flow paths. The fraction of young water up to 7 days (<7 days) is highest in the agricultural lowland headwater catchment (catchment 6; mean: 0.082 or 8.2 %) and lowest in the pristine forested headwater catchment (catchment 3; mean: 0.032 or 3.2 %), considering the mean of all best simulations and the whole time series. In the forested hilly catchment (catchment 5), the contribution of water older than 180 days (>180 days) is highest compared to other catchments (mean: 0.75 or 75 %), which is also reflected by high median transit times (see Figure 7). The hilly anthropogenic and the anthropogenic catchments (catchments 1 and 2, respectively) as well as the agriculturally dominated catchment (catchment 4) have similar proportions of different water ages. The water age contributions of the mountainous agricultural dominated catchment (catchment 4) are in similar ranges as from the hilly anthropogenic (catchment 1) and the anthropogenic (catchment 2) catchments.

The performance of simulated isotopic signature by tran-SAS is shown in Figure 3, in which the black line shows the mean of all best simulations and the red area reflects the variability of all best simulations. For the catchments 1 (hilly, high anthropogenic impact), 4 (mountainous agriculturally dominated), and 5 (forested, hilly), the simulations generally match the observed values (grey dots in Fig. 3), which is also reflected by high KGE values (KGE = 0.65-0.79) and low absolute biases (absolute bias = -0.09 – 0.09). The 10% best simulations for the catchment 3 (pristine forested headwater catchment) show similar KGE values (KGE = 0.63-0.71) but larger biases (absolute bias = -0.58 – 0.49), while for the catchments 2 (high anthropogenic impact) and 6 (agricultural lowland headwater catchment) the KGE is lower (KGE = 0.47-0.54), and the bias is visibly higher (absolute bias = -0.74 – 0.48). In catchments 3,5 and 6, the model tends to overestimate isotopic measurements, which has to be considered for interpreting the results.

3.2 Sensitivity of young water fractions to discharge

Figures 4 and 5 display the discharge sensitivity according to Equ. 9 as black line in each plot, showing positive slope for each catchment. With increasing discharge percentiles, the Fyw60 increases as well, but in different intensities for each catchment. Sd as discharge sensitivity metric (Gallart et al., 2020) is highest in the agriculturally dominated headwater catchment (catchment 6; Sd = 0.232) and lowest in the hilly, forested catchment (catchment 5; Sd = 0.024). The discharge sensitivity of our investigated catchments yielded similar ranges as found in von Freyberg et al. (2018) and Gallart et al. (2020), except for the agriculturally dominated headwater catchment (catchment 6) which showed higher discharge sensitivity than all other catchments (Table 2).

Table 2: Values for F0 and Sd and their standard deviation obtained from Gauss-Newton fitting algorithm using eq. 9 for Fyw7 (water with an age up to 7 days) and Fyw60 (water with an age up to 60 days).

	Fyw7		**Fyw60**	
Catchment	**F0**	**Sd**	**F0**	**Sd**
1	0.043 ± 0.002	0.067 ± 0.005	0.208 ± 0.005	0.069 ± 0.014
2	0.032 ± 0.002	0.036 ± 0.003	0.152 ± 0.006	0.051 ± 0.011
3	0.006 ± 0.001	0.019 ± 0.001	0.092 ± 0.015	0.064 ± 0.010
4	0.034 ± 0.004	0.058 ± 0.011	0.170 ± 0.007	0.087 ± 0.023
5	0.032 ± 0.001	0.028 ± 0.003	0.136 ± 0.002	0.024 ± 0.006
6	0.069 ± 0.004	0.180 ± 0.034	0.218 ± 0.008	0.232 ± 0.087

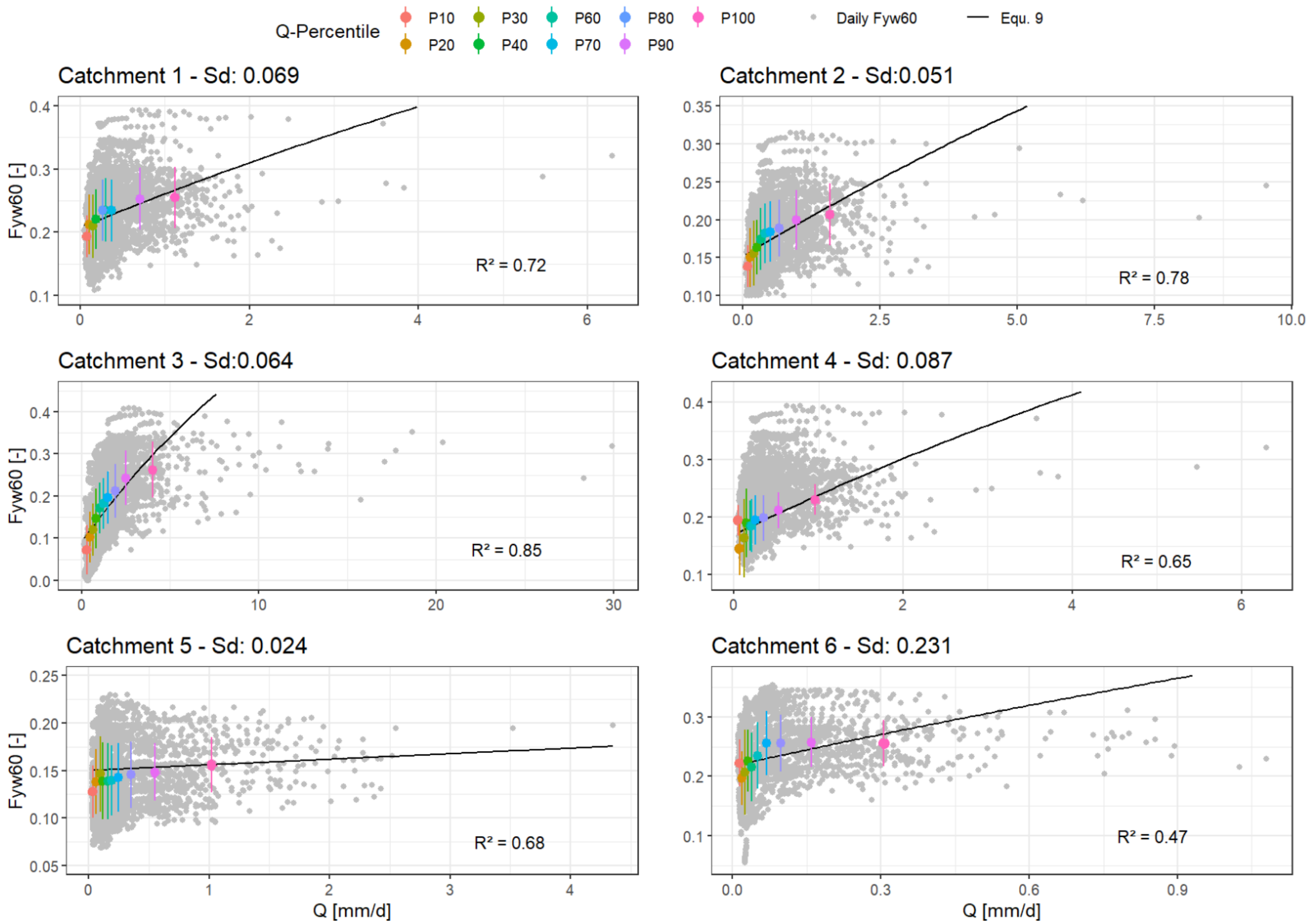


Figure 4: Relationship between discharge and the fraction of water with an age up to 60 days (Fyw60) with the median discharge (Q [mm/d]) from each percentile and the mean Fyw60 as well as its standard deviation from each Q-percentile for the whole time series; Fyw60 of discharge percentiles (P10-P100) are represented as colored points with standard deviation, while the black line represents Equ. 9 to describe the discharge sensitivity (Sd) of the Fyw60; the coefficient of determination (R^2) describes the fit of Equ. 9 on the colored dots.

Considering Fyw7 (Fig. 5), the discharge sensitivity of all catchments is lower compared to the discharge sensitivity of Fyw60 (Fig. 4). For some catchments (i.e., hilly anthropogenic catchment 1 and forested, hilly catchment 5) the difference is small, while for other catchments the difference of the discharge sensitivities is large (pristine forested headwater catchment 3). This means that the Fyw7 is generally less affected by discharge than Fyw60, but it depends on the catchment. Catchments that were characterized by a hilly landscape showed a small difference of the discharge sensitivities of both Fyw7 and Fyw60, while the catchment with the highest discharge showed the largest difference of discharge sensitivities of both Fyw7 and Fyw60. These indications lead us to further investigate catchment's characteristics and their relationship to young water (Fyw7 and Fyw60) in a separate chapter (Chapter 3.5).

While Equ. 9 and the discharge sensitivity metric Sd give information about the average behavior of the fractions of different water ages of each catchment, the daily Fyw7 and Fyw60 (grey dots) give the opportunity to evaluate their variations with respect to the discharge. Most of the catchments show similar patterns: they have discharge sensitivities of Fyw60 which do not differ strongly across catchments, considering the standard deviation (Catchments 1, 2, 3, 4). The anthropogenic catchment (catchment 2) and the pristine forested headwater catchment (catchment 3) show steeper slopes for Fyw60 than for Fyw7, which indicates that Fyw60 is more sensitive to discharge than Fyw7 in these catchments. Catchments with steep slopes of Fyw60 but lower slopes for Fyw7 can be catchments that release water from previous precipitation events (Fyw7) more uniformly, but with increasing discharge the amount of young water up to 60 days is released more dominantly. This is in line with findings from von Freyberg et al. (2018b), who investigated the storm runoff response by using event and pre-event water and found out that predominantly pre-event water from shallow water pathways is released during storm runoff with increasing discharge peaks. In our study, the highest discharge sensitivity was found for the agriculturally dominated headwater catchment, which is the smallest catchment investigated. Probably due to the high amount of agricultural land use and associated tile-drainage systems, the catchment is prone to release young water very quickly, which is in line with the daily Fyw60 and Fyw7 values showing the highest fractions compared to all other catchments.

The release of young water by catchments that are dominated by agricultural land use was also found by Jasechko et al. (2016), who investigated 254 watersheds globally and found out that the streamflow of most of the catchments consists of 30% young water with predominantly higher amounts of young water for agriculturally dominated catchments. Considering the daily Fyw60 and Fyw7, the neighboring catchments (hilly, forested and agriculturally dominated headwater catchments) show a more distributed pattern of the daily Fyw7 and Fyw60 than the other catchments. The high day-to-day variability of different young water fractions indicate that these catchments are more affected by climatic conditions such as dry periods, when water storages that contain more old water can dry out., As a result, more young water is released during high flows after prolonged dry conditions. This assumption is investigated in more detail in the following sections.

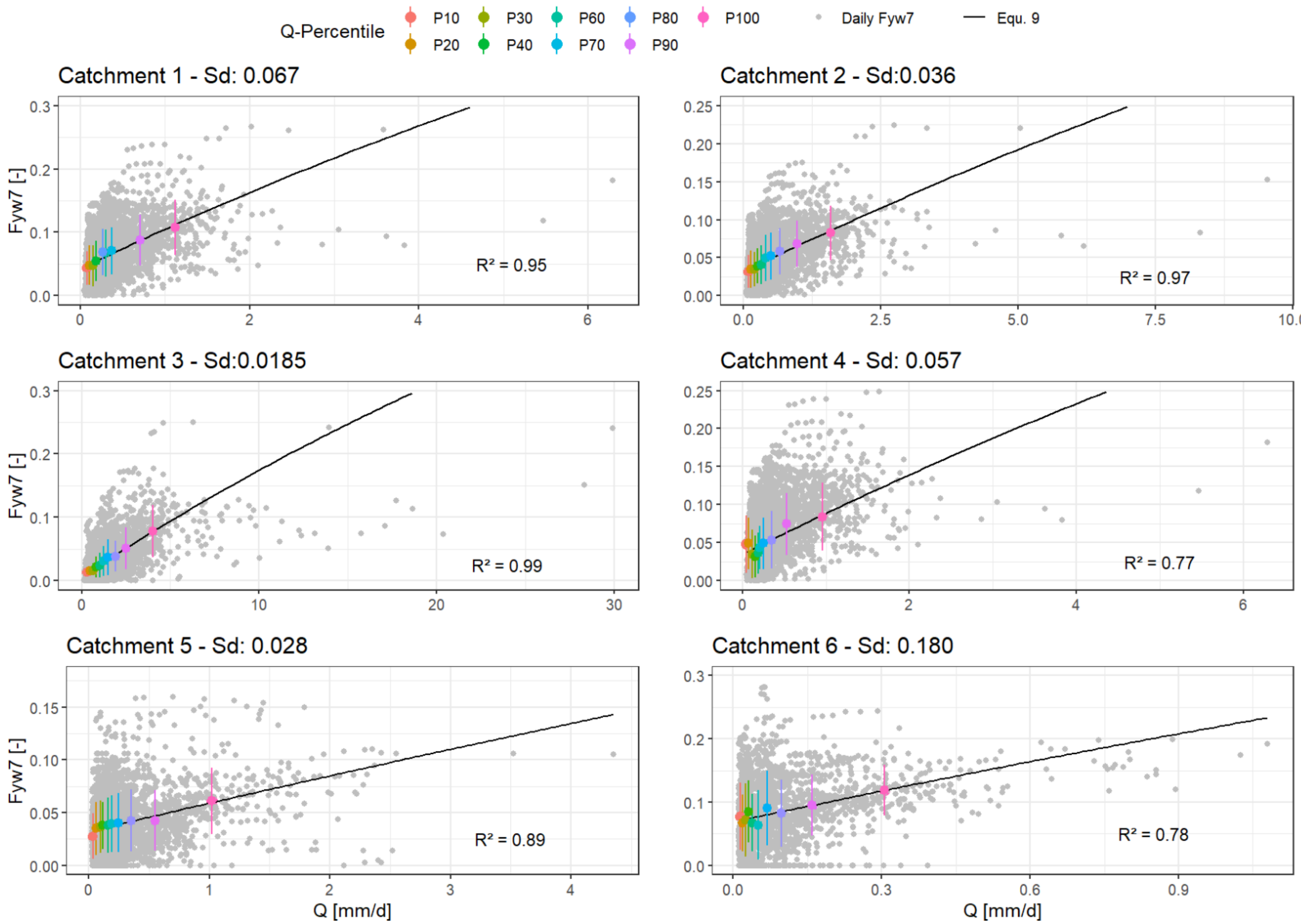


Figure 5: Relationship between discharge and the fraction of water with an age up to 7 days (Fyw7) with the median discharge (Q [mm/d]) from each percentile and the mean Fyw7 as well as its standard deviation from each Q-percentile from the whole time series; Fyw7 of discharge percentiles (P10-P100) are represented as colored points with standard deviation, while the black line represents Equ. 9 to describe the discharge sensitivity (Sd) of the Fyw7; the coefficient of determination (R^2) describes the fit of Equ. 9 on the colored dots.

3.3 The effect of hydrologically divergent periods on discharge age distribution

The discharge sensitivity analysis showed that both Fyw7 and Fyw60 are sensitive to discharge intensities. To better understand how fractions of different water ages are affected during low flows and high flows und to highlight hydrologically divergent periods, the time series was separated into dry and wet spells according to their discharge. The results of this separation and the differences in the number of wet spells between the years and between the single catchment is shown in table 3.

Table 3: The number of wet spells in total and the mean duration of wet spells during the years for the investigated catchments

Catchment	1		2		3		4		5		6	
	Wet Spell	Mean duration	Wet Spell	Mean duration	Wet Spell	Mean duration	Wet Spell	Mean duration	Wet Spell	Mean duration	Wet Spell	Mean duration
Total	43	-	36	-	28	-	10	-	53	-	22	-
Mean	5	74	4	90	3	97	5	65	6	50	3	83
2013	2	132	1	152	1	117	-	-	4	60	1	136
2014	7	65	7	77	4	103	-	-	11	28	7	74
2015	5	56	4	100	3	77	-	-	5	45	2	115
2016	5	72	4	72	4	97	-	-	7	39	2	96
2017	6	64	6	64	4	95	-	-	6	53	6	49
2018	4	80	3	111	2	144	-	-	4	64	1	80
2019	4	55	3	85	3	96	-	-	5	31	2	46
2020	6	58	5	60	4	71	4	70	3	55	1	65
2021	4	84	3	87	3	71	6	60	6	74	-	-

The variation of the mean median transit times (TT50) of all simulations across the study period varies strongly for the different catchments (Fig. 6). Whereas TT50s are the smallest in the hilly anthropogenic catchment (catchment 1) and the pristine forested headwater catchment (catchment 3) with 150 to 450 days, the highest TT50s occur in the neighboring catchments 5 (forested, hilly) and 6 (agricultural lowland headwater) (between 600 and 1000 days). The anthropogenic catchment (catchment 2) and the mountainous agriculturally dominated catchment (catchment 4) are in the middle of the distribution, covering TT50s of between 300 and 600 days. In general, the TT50s are smaller during wet spells compared to dry spells. This illustrates the higher contribution of young water during wet spells compared to dry spells. The Fractions of young water complement this observation by showing a higher Fyw of up to 7 days during wet spells for all the catchments, compared to dry spells and the time series in general. This behavior of more young water holds for all Fyw metrics investigated (i.e., water with an age of up to 14, 28, 60 and 180 days; Fig. 6).

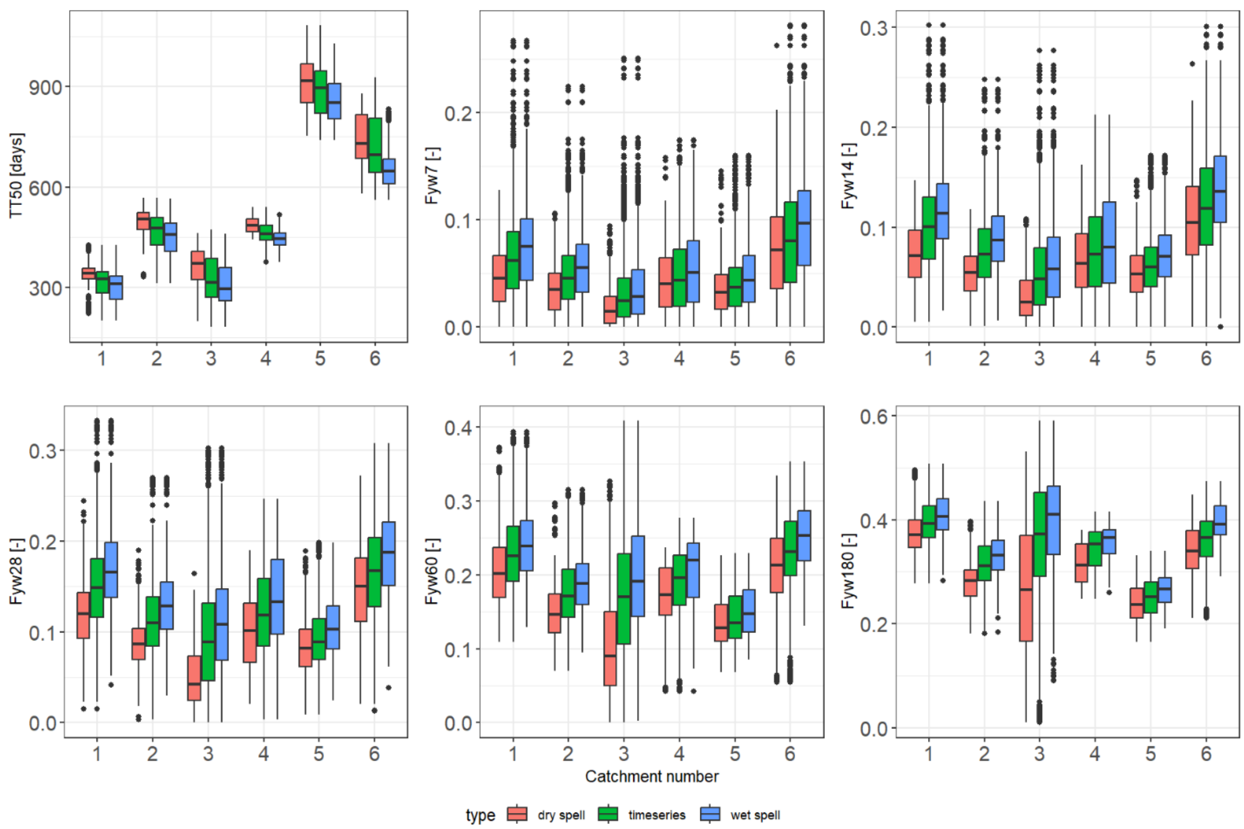


Figure 6: The age metrics (TT50 and Fyw7-180) for each catchment during dry spells (red), the whole time series (green) and wet spells (blue).

The higher proportion of young water during wet spells as seen in Figure 6 becomes also apparent in the different seasons (Figure 7 and 8). All catchments show significantly higher contributions of young water up to 7 days during wet spells compared to dry spells during all seasons ($p<0.05$), except for the mountainous agriculturally dominated catchment (catchment 4) where no significant difference between spring and autumn is obvious. During summer and in some cases during autumn, the relative contribution of Fyw7 to overall discharge is significantly larger than during the other seasons ($p<0.05$), except for hilly catchments 2, 4 and 6 where no significant difference can be found between summer and winter periods. Also, the pristine forested headwater catchment (catchment 3) does not show a significant difference between summer and spring. Especially the neighboring catchments 5 (forested, hilly) and 6 (agricultural lowland headwater) show increasing Fyw7 values during summer and autumn with a significant difference ($p<0.05$) to spring and winter. The mountainous agriculturally dominated catchment (catchment 4), which has the shortest simulation and measurement time series (2020-2021, 2 years), shows a somewhat different pattern with only small differences between the three categories during spring and autumn. In summer and winter, on the contrary, Fyw7 shows the same pattern as in all the other catchments. Considering the time series, Fyw7 is lowest for most of the catchments during spring, while Fyw7 is highest during winter. During summer and autumn, the distribution of Fyw7 is similar across all catchments (Fig. 7: green boxplots).

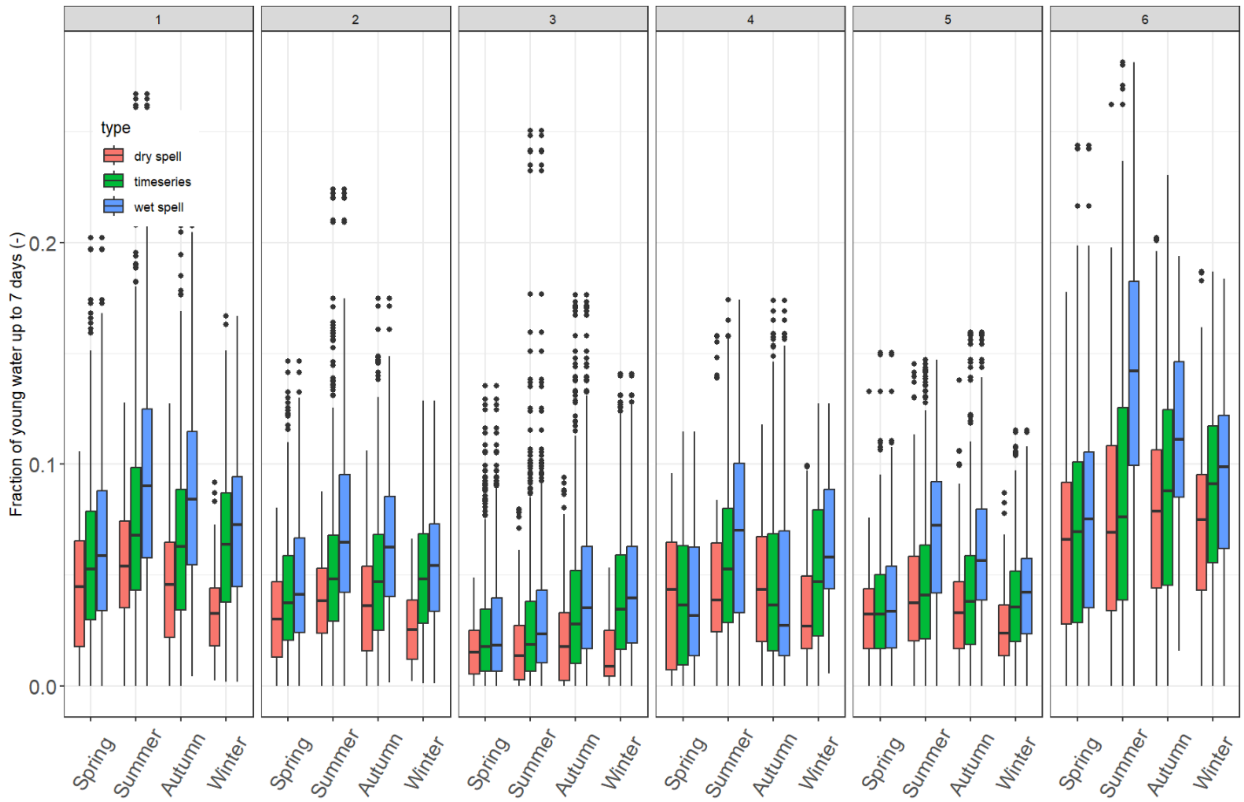


Figure 7: Focusing on the Fyw7 (Fractions of young water up to 7 days), boxplots are plotted for dry spells (red), time series (green) and wet spells (blue) during the seasons (Spring, Summer, Autumn and Winter)

For four out of six catchments a significant difference ($p<0.05$) between the seasons is obvious with respect to Fyw60 (Fig. 8). The anthropogenic catchment (catchment 2) and the agricultural lowland headwater catchment (catchment 6) do not show a significant difference of Fyw60 between the seasons summer and autumn for wet spells, while the mountainous agriculturally dominated catchment (catchment 4) does not show a significant difference of Fyw60 between spring and winter for both wet and dry spells. This implies that catchment 4 has similar sources of water during winter and spring. Likewise, for wet spells in summer, the Fyw60 does not differ significantly from wet spells during spring in the same catchment supporting the assumption that similar water sources are active during these periods. Considering catchment 4 has the shortest observation period, which started in 2020 after the drought years 2018 and 2019, it is most likely that the seasonal differences in Fyw60 that can be seen in the other catchments become apparent because of the longer observation periods that reveal a broader range of different climatic conditions and a more systematic perspective compared to catchment 4. In the anthropogenic catchment (catchment 2), the difference between Fyw60 of dry spells during spring and autumn is not significant.

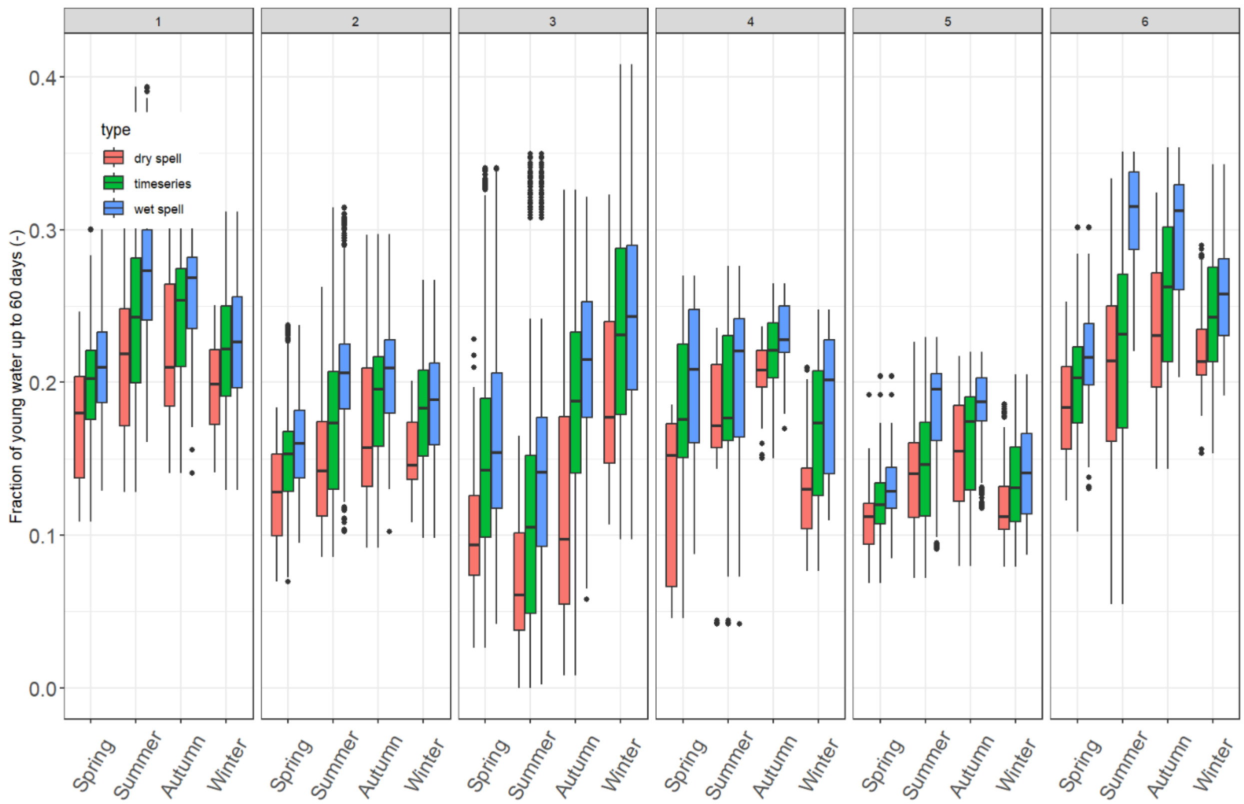


Figure 8: Focusing on the Fyw60 (Fractions of young water up to 60 days), boxplots are plotted for dry spells (red), time series (green) and wet spells (blue) during the seasons (Spring, Summer, Autumn and Winter)

In agreement with a conceptual perspective, the findings of our study match the common expectations that higher contributions of young water (Fyw7 and Fyw60) were found for wet spells than for dry spells. While this behavior was occurring throughout the time series from 2013 to 2021 for all the six catchments that have been investigated, a much higher contribution of Fyw7 during summer wet spells was found for two of the six catchments. In the agricultural lowland headwater catchment (catchment 6) as well as in the forested, hilly catchment (catchment 5), Fyw7 was higher compared to the other seasons, which indicates that wet spells with high discharge during summer are mainly fed by recent precipitation events. These observations are in line with findings from other studies (Brown, McDonnell et al. 1999, Lee, Shih et al. 2020). Brown et al. (1999) investigated five summer rain events in seven different catchments with the aim to evaluate the storm runoff components and the effect of catchment size on water sources. Using a two-component hydrograph separation to analyze the contribution of water sources during rain events, they were able to show that there were high event water contributions to stormflow for the most intense event and that during dry spells event water is a major contributor to stormflow. Lee et al. (2020) analyzed six typhoons during a 3-year period and found out that higher rainfall intensity causes a higher amount of event water which lowers the mean transit time (MTT).

3.4 Catchment characteristics influence extent of discharge age distribution

A comparison of the relationship between different land use types (agriculture, forest, grassland and urban) and Fyw7 revealed trends for agriculture and grassland depending on their relative proportions (Figure 9). With increasing agricultural land use share the Fyw7 increases significantly ($p<0.05$, $R^2=0.82$; Fig. 9) while the Fyw7 increases when the proportion of grassland decreases in catchments ($p>0.05$, $R^2=0.90$; Fig. 9). Considering the urban land use share, the pattern and trend is similar to the one of agricultural land use share: here again the Fyw7 increases with increasing urban land use share ($p>0.05$, $R^2=0.56$; Fig. 9). For catchment characteristics such as catchment area, slope, gradient, baseflow index, mean elevation and flow path length, significant yet unsystematic differences of the Fyw7 for the different catchments were found (Supp. Fig. 1). For the anthropogenic catchment (catchment 2) and the mountainous agriculturally dominated catchment (catchment 4) the differences of Fyw7 according to their mean elevation, catchment area, gradient, flow path length and baseflow index were not significant.

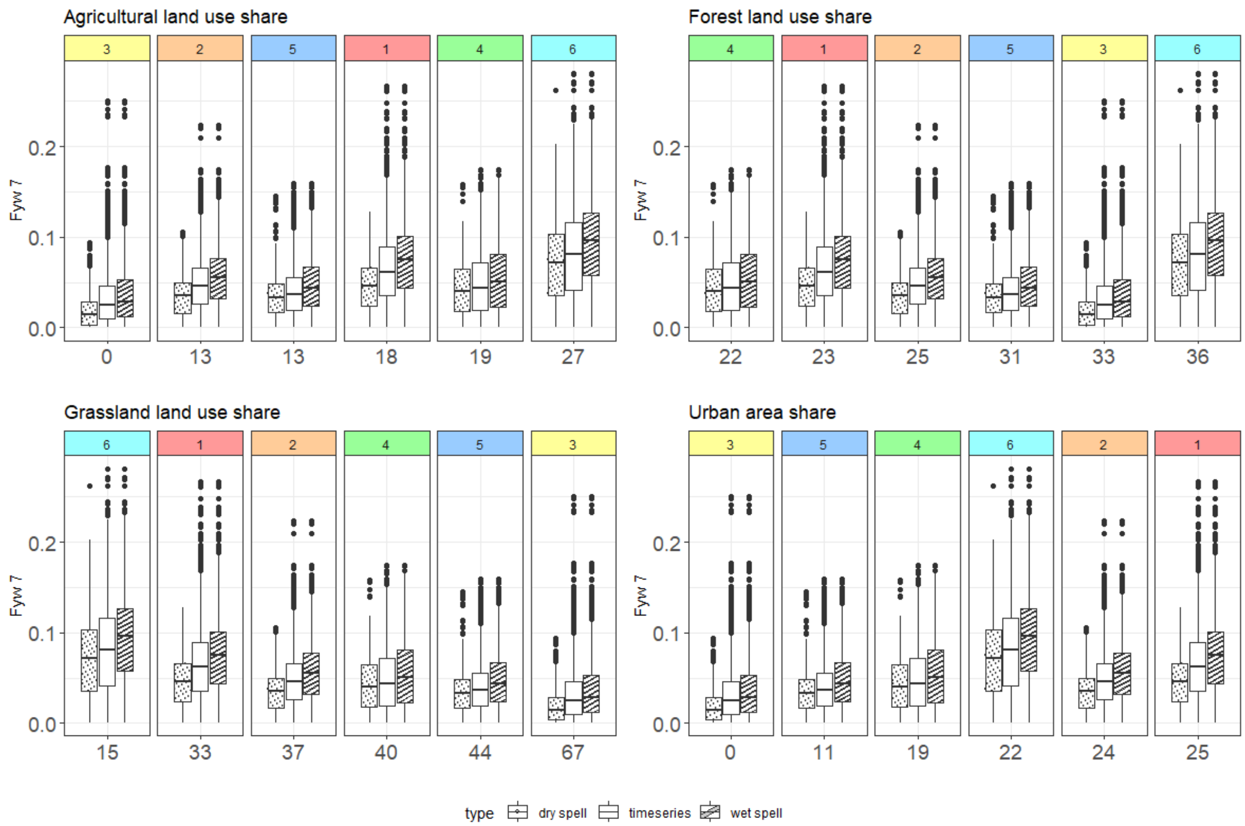


Figure 9: Fyw7 for different catchment characteristics (land use share [%]: agriculture, forest, grassland and urban area) with boxplots representing dry spells (dots), the entire time series (blank) and wet spells (stripes).

For Fyw60, the pattern of increasing fraction of young water with increasing agricultural land use share as well as the increasing fraction of young water with decreasing grassland proportion is not as strong as for Fyw7, but still present (R^2: agriculture = 0.55; grassland = 0.41) (Fig. 10). This suggests that the release of water from previous rainfall events, such as Fyw7 is more dependent on land use and land cover characteristics than Fyw60. Hence, one can assume that agriculturally dominated catchments are in general more sensitive to short term precipitation events as agriculturally dominated catchments release predominantly young water from recent precipitation rather than from deeper water sources, which is supported by results from Jasechko et al. (2016), who found out that agriculturally dominated catchments release more young water than catchments with other landscape characteristics.

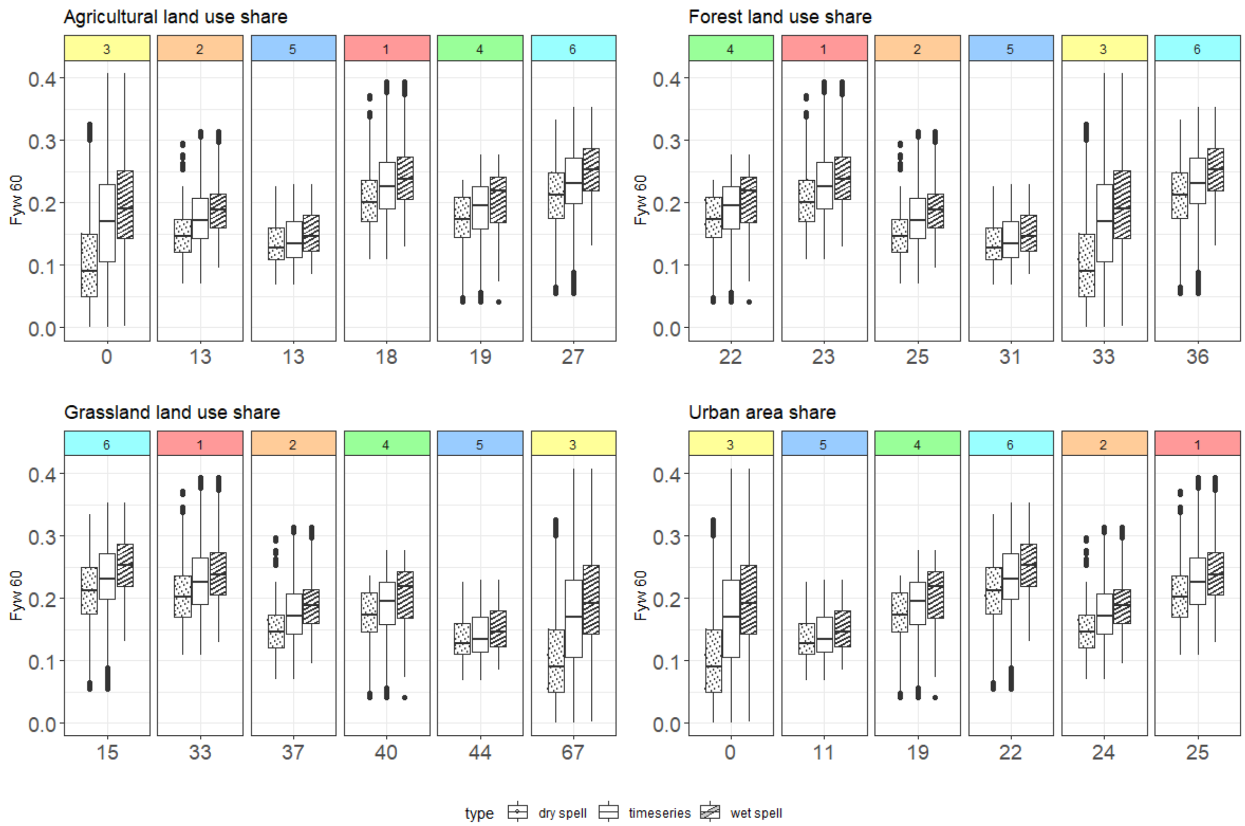


Figure 10: Fyw60 for different catchment characteristics (land use share [%]: agriculture, forest, grassland and urban area) with boxplots representing dry spells (dots), the entire time series (blank) and wet spells (stripes).

Our data suggests that there is no direct relation between Fyw7 and the catchment area. This is in line with other studies that did not find a relation between transit time metrics and catchment area (Brown, McDonnell et al. 1999, Tetzlaff, Seibert et al. 2009, Lutz, Krieg et al. 2018, Lee, Shih et al. 2020). While Jutebring Sterte, Lidman et al. (2021) were able to show a relationship between the catchment size and MTT as well as Fyw up to 2-3 months, they highlighted that the catchment size is only correlating with the age metrics due to soil types with low conductive silty sediments and the areal coverage of mires. To analyze the sensitivity of young water up to 2-3 months to hydro-climatic forcing and landscape properties, von Freyberg, Allen et al. (2018a) investigated 22 Swiss catchments with catchment areas ranging from 0.7 to 351 km². They revealed that the catchment area correlated with Fyw only with the lower elevation catchments and the catchments that are not dominated by snow. However, they found a relationship between Fyw and the areal fraction of saturated soils and low permeability soils which is in line with the findings from Dimitrova-Petrova et al. (2020) and Jutebring Sterte, Lidman et al. (2021). Considering the six catchments of our study, they have a broad variety of different soil types such as luvisols, brown earth, chernozem, gley and sub-types mainly dominated by loess and clay as well as silt; all of these soil types have a low permeability. Lutz, Krieg et al. (2018) already investigated the relationship between water age metrics and catchment characteristics such as soil types, flow path length, catchment area and other catchment characteristics in the Bode region, where our study is conducted as well. They found out that there is no relationship between the catchment characteristics and the Fyw up to 2-3 months during the observed time series from 2013 to 2015. In our study, a weak relationship between Fyw60 and land use types such as grassland and agriculture has been found for the six selected catchments, but for other catchment characteristics such as slope, gradient, mean elevation, flow path length and catchment area we did not find a relation either. Our analysis revealed a positive trend of increasing fractions of young water up to 7 days for an increasing share of agricultural fields with respect to a maximum of agricultural land use about 27 %, whereas a negative trend was found for Fyw7 with an increasing share of grassland, considering that maximum grassland share is 67 % in the investigated catchments. These relationships are stronger for Fyw7 than for Fyw60 in our catchments.

A positive relation between agricultural land use share and increasing Fyw has also been found by Jasechko et al. (2016), who investigated 254 catchments globally in terms of the contribution of Fyw in stream networks. Agricultural land is mainly different from grassland with respect to soil cultivation and the plant cultures growing on the fields. To maintain a plant-favorable soil environment by directing water from rain events immediately from fields to streams, drainage pipes are built in many cases. By this, the travel time of water through the system is shortened. In other studies, a relation between the drainage density and water age metrics such as MTT and Fyw up to 2-3 months was found (Soulsby, Tetzlaff et al. 2010, von Freyberg, Allen et al. 2018, Dimitrova-Petrova et al., 2020). It is thus possible that the drainage network causes the positive relationship between agricultural land use share and the fraction of Fyw7. Since water table management is not mandatory for cultivated grassland used as meadows as well as for grassland that is part of environmental protection areas, the density of artificial drains in such grassland areas is often low or non-existent. By this, grassland areas can hold back more water (from recent precipitation events) before it is released to the stream network (Zhang & Yang, 2022).

Therefore, the decreasing trend of Fyw7 with increasing grassland share in catchments is most likely caused by the buffer capacity of the meadows, mires and environmental protection areas. Since underlying geology has an influence on the landscape structure as well as elevation, it cannot be ruled out that there might be a co-relationship that governs the visible relationship between the land use and Fyw7. Combing the information from all investigated catchments, we did not find any correlation between the contribution of Fyw7 and catchment characteristics such as the slope, elevation or gradient. Despite the missing correlation, we found significant differences of Fyw7 for all catchments that are in turn quite divers with respect to their natural catchment properties like slopes, gradients and mean elevations. To gain more insights into the systematics of the relationship between Fyw7 and catchment characteristics, more detailed information about catchments such as drainage intensity as well as an extended catchment intercomparison study with more investigation areas in different locations from different climatic regions seem necessary.

4 Conclusions

An elaborate high-frequency water isotope monitoring program of stream flow and precipitation was conducted in six different catchments in the Harz mountains and the adjacent northern lowlands, Germany, in order to investigate the relation between age metrics (fractions of different water ages, transit times) and catchment characteristics (discharge, landscape structure metrics). Special focus was put on hydrological divergent periods. Water age metrics are obtained by the tran-SAS model (Benettin and Bertuzzo, 2018) with daily input data. Discharge sensitivities of water parcels with an age of up to 7 and 60 days were obtained using the approach after Gallart et al. (2020), revealing the highest sensitivity for an agriculturally dominated headwater catchment. Generally, agriculturally dominated catchments are likely to release more young water (Jasechko et al., 2016). Consequently, in the context of pollution awareness and pollution control, special attention should be paid to those catchments that are characterized by high shares of agricultural area. This is due to the fact that pollutants (e.g. pesticides) and other solutes (nutrients) can quickly reach the streams with higher fractions of young water. Resulting short transit times may not sustain natural retention or degradation of contaminants posing a potential risk to the streams as the primary receptors of young water shares. With increasing share of grassland, Fyw7 decreases, which indicates that landscape structures affect the hydrological conditions of streams. Probably, higher amounts of grassland as well as more grassland patches between agricultural fields could have a reverse effect on the release of young water by holding back younger water proportions and supporting the infiltration to deeper storages. This might create a positive side effect with respect to pollution control by facilitating longer travel times and, as a consequence, an enhanced pollutant degradation potential. However, especially in Central and Western Europe, climate change impacts will result in more frequent rainfall events after prolonged dry conditions leading to a scenario with more dominant release of young water increasing the pollution risk of the streams. The assumption of such a scenario is supported by the findings of this study with respect to increasing amounts of young water, both Fyw60 and Fyw7, from summer to autumn. This behavior might result from the catchment storage drying out during prolonged dry spells resulting in less mixing between water sources in the subsurface. Catchments with high discharge peaks were prone to have lower discharge sensitivities for Fyw7 compared to Fyw60, indicating that these catchments are more affected by increasing discharge and react more quickly to increasing discharge with higher fractions of young water from preceding precipitation. As expected, the analysis of high and low flows revealed higher contributions of young water during wet spells compared to dry spells considering daily data of each wet/ dry spell.

Considering their large potential variability on a regional or even global scale, the hydro-climatic properties of the six investigated catchments were in a quite narrow range. To some extent, this hampers the recognition of the systematic relationships between catchment characteristics and fractions of young water. We believe that significant additional knowledge gain can be expected if the selected catchments reflect a much broader range of catchment characteristics and hydro-climatic properties knowing though that such an approach would be associated with enormous logistical challenges. However, one of the valuable contributions of our study is that it could serve as a blueprint for further investigations aiming at the recognition of hydrological processes and the age distribution of stream water during divergent hydrological periods in a more global context. Upcoming studies should in particular pay attention to the differing tendency of catchments to release water from previous precipitation events and water that is categorized as young water with an age around 2-3 months as this young water share carries the main pollution risk.

Understanding how catchments react during differing hydrological conditions and the implementation of this understanding into land management actions is crucial for controlling nutrient losses and pollution risks of streams especially in the view of the projected climate change. As shown by this study, high-frequency isotope monitoring programs in concert with the application of appropriate transit time models can significantly contribute to enlarge this understanding.

Acknowledgments

There is no conflict of interest for any author.

Monitoring set up was implemented by KK and CM. Samples were collected by KK and CM, while sample preparation and laboratory isotope analysis were conducted by CR and laboratory staff of the Helmholtz-Centre for Environmental Research in Halle, Germany. The study was developed by CR, KK, SL and RM. The mHM-model was set up and run by RK, while the tran-SAS models for each catchment were set up und run by CR. Data analysis (statistics, discharge sensitivity) was conducted by CR. The manuscript was written by CR, while all other co-authors reviewed the manuscript.

We are grateful for the support by Jana von Freyberg, who gave helpful advice on the implementation of the discharge sensitivity approach for fractions of young water derived from tran-SAS. We would like to thank Paolo Benettin for being the contact person in terms of questions with regard to the tran-SAS v1.0 model.

Open Research

Datasets including isotope measurements and the mHM-simulations of all six catchments are stored for the purposes of peer review process at the UFZ-nextcloud accessible via the following link and password: https://nc.ufz.de/s/yz6pMACGFikaxKx ,password: *WRR_23_Radtke*. By the time the article is accepted the data will be made publicy available with a DOI via the datainvestigationportal of the Helmholtz-Centre for Environmental Research (https://www.ufz.de/drp/en/). Water age metrics can be derived using the tran-SAS model (Benettin & Bertuzzo, 2018: https://doi.org/10.5194/gmd-11-1627-2018 (article) and https://github.com/pbenettin/tran-SAS (source code)) with the data provided and the parameters mentioned in the paper.

References

BGR. (2020). Bodenübersichtskarte. Bundesanstalt für Geowissenschaften und Rohstoffe.

BGR. (2020). Hydrogeologische Übersichtskarte. Bundesanstalt für Geowissenschaften und Rohstoffe.

Benettin, P. and E. Bertuzzo (2018). "tran-SAS v1.0: a numerical model to compute catchment-scale hydrologic transport using StorAge Selection functions." Geoscientific Model Development 11(4): 1627-1639.

Borriero, A., Kumar, R., Nguyen, T. V., Fleckenstein, J. H., and Lutz, S. R.: Uncertainty in water transit time estimation with StorAge Selection functions and tracer data interpolation, Hydrol. Earth Syst. Sci. Discuss. [preprint], https://doi.org/10.5194/hess-2022-222, in review, 2022.

Brown, V. A., J. J. McDonnell, D. A. Burns and C. Kendall (1999). "The role of event water, a rapid shallow flow component, and catchment size in summer stormflow." Journal of Hydrology.

Dimitrova-Petrova, K., J. Geris, M. E. Wilkinson, A. Lilly and C. Soulsby (2020). "Using isotopes to understand the evolution of water ages in disturbed mixed land-use catchments." Hydrological Processes 34(4): 972-990.

DWD Climate Data Center (CDC): Historische tägliche Stationsbeobachtungen (Temperatur, Druck, Niederschlag, Sonnenscheindauer, etc.) für Deutschland, Version v21.3, 2021.

GeoBasis-DE / BKG. (2013). Elevation data 200m resolution. Bundesamt für Kartographie und Geodäsie.

GeoBasis-DE / BKG. (2018). Land-use data. Bundesamt für Kartographie und Geodäsie.

Gupta, H. V., H. Kling, K. K. Yilmaz and G. F. Martinez (2009). "Decomposition of the mean squared error and NSE performance criteria: Implications for improving hydrological modelling." Journal of Hydrology 377(1-2): 80-91.

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 Resources Research 45(5).

Jasechko, S., J. W. Kirchner, J. M. Welker and J. J. McDonnell (2016). "Substantial proportion of global streamflow less than three months old." Nature Geoscience 9(2): 126-129.

Jutebring Sterte, E., F. Lidman, E. Lindborg, Y. Sjöberg and H. Laudon (2021). "How catchment characteristics influence hydrological pathways and travel times in a boreal landscape." Hydrology and Earth System Sciences 25(4): 2133-2158.

Kaur, S., A. Horne, M. J. Stewardson, R. Nathan, A. M. Costa, J. M. Szemis and J. A. Webb (2017). "Challenges for determining frequency of high flow spells for varying thresholds in environmental flows programmes." Journal of Ecohydraulics 2(1): 28-37.

Kirchner, J. W. (2016a). "Aggregation in environmental systems – Part 1: Seasonal tracer cycles quantify young water fractions, but not mean transit times, in spatially heterogeneous catchments." Hydrology and Earth System Sciences 20(1): 279-297.

Kirchner, J. W. (2016b). "Aggregation in environmental systems – Part 2: Catchment mean transit times and young water fractions under hydrologic nonstationarity." Hydrology and Earth System Sciences 20(1): 299-328.

Kirchner, J. (2018). "Quantifying new water fractions and transit time distributions using ensemble hydrograph separation: theory and benchmark tests." Hydrol Earth Syst Sci.

Knapp, J. L. A., Neal, C., Schlumpf, A., Neal, M., and Kirchner, J. W. (2019): New water fractions and transit time distributions at Plynlimon, Wales, estimated from stable water isotopes in precipitation and streamflow, Hydrol. Earth Syst. Sci., 23, 4367–4388, https://doi.org/10.5194/hess-23-4367-2019.

Kumar, R., L. Samaniego and S. Attinger (2013). "Implications of distributed hydrologic model parameterization on water fluxes at multiple scales and locations." Water Resources Research.

Kundzewicz, Z. W., S. Kanae, S. I. Seneviratne, J. Handmer, N. Nicholls, P. Peduzzi, R. Mechler, L. M. Bouwer, N. Arnell, K. Mach, R. Muir-Wood, G. R. Brakenridge, W. Kron, G. Benito, Y. Honda, K. Takahashi and B. Sherstyukov (2013). "Flood risk and climate change: global and regional perspectives." Hydrological Sciences Journal 59(1): 1-28.

Kuppel, S., D. Tetzlaff, M. P. Maneta and C. Soulsby (2018). "EcH^{2}O-iso 1.0: water isotopes and age tracking in a process-based, distributed ecohydrological model." Geoscientific Model Development 11(7): 3045-3069.

Ladson, A. R., R. Brown, B. Neal and R. Nathan (2013). "A standard approach to baseflow separation using the Lyne and Hollick filter." Australian Journal of Water Resources 17(1).

Landesbetrieb für Hochwasserschutz und Wasserwirtschaft. (10. 10 2022). *Hochwasservorhersagezentrale.* Von https://hochwasservorhersage.sachsen-anhalt.de/messwerte/durchfluss/?no_cache=1 abgerufen

Lang, M., T. B. M. J. Ouarda, and B. Bobée (1999), Towards operational guidelines for over-threshold modeling, J. Hydrol., 225, 103– 117.

Lee, J.-Y., Y.-T. Shih, C.-Y. Lan, T.-Y. Lee, T.-R. Peng, C.-T. Lee and J.-C. Huang (2020). "Rainstorm Magnitude Likely Regulates Event Water Fraction and Its Transit Time in Mesoscale Mountainous Catchments: Implication for Modelling Parameterization." Water 12(4).

Lutz, S. R., R. Krieg, C. Müller, M. Zink, K. Knöller, L. Samaniego and R. Merz (2018). "Spatial Patterns of Water Age: Using Young Water Fractions to Improve the Characterization of Transit Times in Contrasting Catchments." Water Resources Research 54(7): 4767-4784.

Lyne, V. and M. Hollick (1979). "Stochastic Time-Variable Rainfall Runoff Modelling." Institute of Engineers Australia National Conference.

Lyon, S. W., S. W. Ploum, Y. van der Velde, G. Rocher-Ros, C.-M. Mörth and R. Giesler (2018). "Lessons learned from monitoring the stable water isotopic variability in precipitation and streamflow across a snow-dominated subarctic catchment." Arctic, Antarctic, and Alpine Research 50(1).

Merz, R., Blöschl, G., & Parajka, J. (2006). Spatio-temporal variability of event runoff coefficients. Journal of Hydrology, 331(3–4), 591–604. http://doi.org/10.1016/j.jhydrol.2006.06.008

Michelsen, N., G. Laube, J. Friesen, S. Weise, A. Said and T. Müller (2019). „Technical note: A microcontroller-based automatic rain sampler for stable isotope studies". Hydrology and Earth System Sciences. 23. 2637-2645.

Mueller, C., Zink, M., Samaniego, L., Krieg, R., Merz, R., Rode, M. and Knöller, K., 2016. Discharge driven nitrogen dynamics in a mesoscale river basin as constrained by stable isotope patterns. Environmental Science & Technology, 50(17), pp.9187-9196.

Samaniego, L., R. Kumar and S. Attinger (2010). "Multiscale parameter regionalization of a grid-based hydrologic model at the mesoscale." Water Resources Research.

Sikorska, A. E., Viviroli, D., & Seibert, J. (2015). Flood-type classification in mountainous catchments using crisp and fuzzy decision trees. Water Resources Research, 51(10), 7959–7976. http://doi.org/10.1002/2015WR017326

Soulsby, C., D. Tetzlaff and M. Hrachowitz (2010). "Are transit times useful process-based tools for flow prediction and classification in ungauged basins in montane regions?" Hydrological Processes.

Soulsby, C., D. Tetzlaff, P. Rodgers, S. Dunn and S. Waldron (2006). "Runoff processes, stream water residence times and controlling landscape characteristics in a mesoscale catchment: An initial evaluation." Journal of Hydrology 325(1-4): 197-221.

Stockinger, M. P., H. R. Bogena, A. Lücke, B. Diekkrüger, T. Cornelissen and H. Vereecken (2016). "Tracer sampling frequency influences estimates of young water fraction and streamwater transit time distribution." Journal of Hydrology 541: 952-964.

Tang, W. and S. K. Carey (2017). "HydRun: A MATLAB toolbox for rainfall-runoff analysis." Hydrological Processes 31(15): 2670-2682.

Tetzlaff, D., J. Seibert, K. J. McGuire, H. Laudon, D. A. Burns, S. M. Dunn and C. Soulsby (2009). "How does landscape structure influence catchment transit time across different geomorphic provinces?" Hydrological Processes 23(6): 945-953.

von Freyberg, J., B. Studer and J. W. Kirchner (2017). "A lab in the field: high-frequency analysis of water quality and stable isotopes in stream water and precipitation." Hydrology and Earth System Sciences 21(3): 1721-1739.

von Freyberg, J., S. T. Allen, S. Seeger, M. Weiler and J. W. Kirchner (2018a). "Sensitivity of young water fractions to hydro-climatic forcing and landscape properties across 22 Swiss catchments." Hydrology and Earth System Sciences 22(7): 3841-3861.

von Freyberg, J., B. Studer, M. Rinderer and J. W. Kirchner (2018b). "Studying catchment storm response using event- and pre-event-water volumes as fractions of precipitation rather than discharge." Hydrology and Earth System Sciences 22(11): 5847-5865. https://doi.org/10.5194/hess-22-5847-2018

Wilusz, D. C., C. J. Harman and W. P. Ball (2017). "Sensitivity of Catchment Transit Times to Rainfall Variability Under Present and Future Climates." Water Resources Research 53(12): 10231-10256.

Wollschläger, U., S. Attinger, D. Borchardt, M. Brauns, M. Cuntz, P. Dietrich, J. H. Fleckenstein, K. Friese, J. Friesen, A. Harpke, A. Hildebrandt, G. Jäckel, N. Kamjunke, K. Knöller, S. Kögler, O. Kolditz, R. Krieg, R. Kumar, A. Lausch, M. Liess, A. Marx, R. Merz, C. Mueller, A. Musolff, H. Norf, S. E. Oswald, C. Rebmann, F. Reinstorf, M. Rode, K. Rink, K. Rinke, L. Samaniego, M. Vieweg, H.-J. Vogel, M. Weitere, U. Werban, M. Zink and S. Zacharias (2016). "The Bode hydrological observatory: a platform for integrated, interdisciplinary hydro-ecological research within the TERENO Harz/Central German Lowland Observatory." Environmental Earth Sciences 76(1).

Zhang, L.; Yang, F. “Spatio-Temporal Dynamics of Water Conservation Service of Ecosystems in the Zhejiang Greater Bay Area and Its Impact Factors Analysis.” Sustainability 2022, 14, 10392. https://doi.org/10.3390/ su141610392

Zink, M., Kumar, R., Cuntz, M., and Samaniego, L.: A high-resolution dataset of water fluxes and states for Germany accounting for parametric uncertainty, Hydrol. Earth Syst. Sci., 21, 1769–1790, https://doi.org/10.5194/hess-21-1769-2017, 2017.