Investigating young water fractions in a small Mediterranean mountain catchment: both precipitation forcing and sampling frequency matter.

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Abstract

The proportion of water younger than 2-3 months (young water fraction, F_{yw}) has become increasingly investigated in catchment hydrology. F_{yw} is typically estimated by comparing seasonal tracer cycles in precipitation and streamflow, through water sampling. However, some open research questions remain, such as: (i) whether part of the summer precipitation should be discarded because the high evapotranspiration demand, (ii) how well F_{yw} serves as a metric to compare catchments, and (iii) how sampling frequency affects F_{yw} estimates. To address these questions, we investigated F_{yw} in soil-, ground- and stream waters for the small Mediterranean Can Vila catchment. Rainfall was sampled at 5-mm intervals. Mobile soil water and groundwater were sampled fortnightly. Stream water was sampled depending on flow at variable time intervals (30 minutes to 1 week). Over 58 months, this sampling provided 1,529 $\delta^{18}\text{O}$ determinations.

Isotopic analyses results led us to include summer precipitation in the input signal. We found the highest F_{yw} in mobile soil waters (34%), while this was almost zero for groundwater except during wet periods. For stream waters, F_{yw} depended on the discharge variations, so that the flow-weighted young water fraction (F_{yw}^*) was 22.6%, whereas the time-weighted F_{yw} was just 6.2%. Both F_{yw}^* and its discharge sensitivity (S_d) varied when different 12-month sampling periods were investigated. The young water fraction that would be obtained from a virtual thorough sampling (F_{yw}^{**}) was estimated from the S_d and the observed stream flow. This showed an underestimation of F_{yw}^{**} by 25% for the frequent dynamic sampling and 66% for weekly sampling, due to missing high flows. Our results confirm that F_{yw} and its discharge sensitivity are metrics very sensitive to meteorological forcing during the analysed period.

Thus, comparisons between catchments need long-term mean annual values and their variability. Our findings also support the dependence of F_{yw} estimates on the sampling rate and show the advantages of flow-weighted analysis. Finally, catchment water turnover investigations should be accompanied by the analysis of flow duration curves.

1. Introduction

Since the pioneering study by Maloszewski, Rauert, Stichler & Herrmann (1983), the comparison between the seasonal variation of stable isotopes (^2H and ^{18}O) of precipitation and stream waters, with either the convolution integral or sinusoid fitting applied, has been used to investigate the turnover time of water in catchments. Mean transit times (MTT) and transit time distributions (TTD) of catchment waters have been intensively investigated for over three decades using these methods (McGuire & McDonnell, 2006), despite limitations of stable isotopes for water fractions that are more than a few years old (Stewart, Morgenstern & McDonnell, 2010; Stewart, Morgenstern, McDonnell & Pfister, 2012).

More recently, Kirchner (2016a) demonstrated that MTT determinations with these methods may be inadequate, especially when waters of different ages mix along their flow paths within catchments. Kirchner (2016a) proposed an alternative water age metric, the ‘fraction of young water’ (F_{yw}), defined as the portion of water that is younger than a threshold age. This fraction can be robustly estimated for a wide range of TTDs, with a threshold age ranging between two and three months, depending on the TTD. Young water fractions have been subject to several recent developments and applications, leading to numerous questions regarding the methods’ specifics, the quality of the F_{yw} estimates and their relationship to hydrological processes. We can group these questions under four main topics frequently mentioned in the literature: the water recharge assumption, the identifiability of catchment F_{yw} , the choice of sampling rate and the behaviour of mountain catchments. We briefly outline the four issues here:

1.1 How should summer precipitation be taken into account (i.e., effective precipitation) for F_{yw} and MTT determinations when using stable isotopes of water?

In a seasonal climate, precipitation (or throughfall) is more enriched in heavy water isotopes during summer than during winter (Allen *et al.*, 2019a), while evapotranspirative demand is higher in summer than in winter. Consequently, a higher portion of summer precipitation might be evapotranspired than precipitation in colder months, before percolating to supply

groundwater and runoff. As a result, the isotope ratios of the infiltrating rain becoming recharge (“effective precipitation”) will probably be biased towards cold/dormant season precipitation (Jasechko *et al.*, 2014), and its seasonal oscillation will be more attenuated than that of precipitation. However, there is no consensus on how this issue (“the recharge assumption” in McGuire & McDonnell, 2006) is to be handled.

A first approach to effective precipitation is to weight the sampled isotope ratio by ‘precipitation minus evapotranspiration’ instead of precipitation. This is habitually obtained by means of a conceptual soil water-balance or precipitation loss (sub-) model before or at the beginning of the modelling exercise or data analysis (*e.g.* Dunn, McDonnell & Vaché, 2007; Lutz *et al.*, 2018; Stewart *et al.*, 2007; Stockinger *et al.*, 2016; Weiler, McGlynn, McGuire & McDonnell, 2003). This approach assumes that evapotranspiration is composed of the latest precipitation at the sampling/modelling time step. However, summer evapotranspiration may consume soil water that is several months old, as isotope data suggest (Allen *et al.*, 2019b; Brooks, Barnard, Coulombe & McDonnell, 2010; Sprenger, Llorens, Cayuela, Gallart & Latron, 2019a). This may overestimate the evapotranspiration losses from summer precipitation.

A second approach accounts for the isotope ratio and age dynamics of the evapotranspiration flux: both are simulated with those of runoff to update the isotope ratio and age distributions of the catchment storage. This approach is used in StorAge Selection (SAS) modelling (van de Velde *et al.*, 2012; Benettin *et al.*, 2017; Harman, 2015) and other flow tracking models (Soulsby *et al.*, 2015; Soulsby, Birkel & Tetzlaff, 2016).

A third approach performs mass balance-based equations of diverse flows and compartments (precipitation, runoff, groundwater, evapotranspiration) between seasons to assess the share of precipitation in these partitions (Grabczak, Maloszewski, Rozanski & Zuber, 1984; Maloszewski, Rauert, Stichler & Herrmann, 1992; Jasechko *et al.*, 2014; Kirchner & Allen, 2020). The advantage of this approach is that it does not need assumptions (beyond the conservation of the tracers and a null balance of the storage) or parameters. Therefore, its uncertainty is only related to the quality of observations (measurement accuracies of rainfall-runoff volumes and its isotope ratios) and to the differences of tracer concentrations between the various compartments and seasons.

Finally, some authors do not claim to take into account this possible effect and use the gross isotopic signature of precipitation waters (or throughfall or melting) as input to the hydrologic system (e.g. von Freyberg, Allen, Seeger, Weiler & Kirchner, 2018; Stockinger, Bogen, Lücke, Stump & Vereecken, 2019; Jacobs *et al.*, 2018), although Lutz *et al.* (2018) refrained from considering evapotranspiration in the weighting of the isotope values in precipitation because the effective rainfall model that they used showed minor differences between the two signatures.

1.2 Can F_{yw} serve as a metric to compare the hydrological behaviour of catchments?

One of the expected applications of F_{yw} in catchments is as a metric for catchment comparison (Kirchner 2016a, b; von Freyberg *et al.*, 2018; Jasechko *et al.*, 2016; Lutz *et al.*, 2018). Nevertheless, F_{yw} is often unsteady and meteorological forcing seems to overwhelm catchment physiographic characteristics: F_{yw} is known to usually increase with stream discharge due to the activation of faster flow paths when the catchment becomes wetter (Kirchner 2016a, b; von Freyberg *et al.*, 2018; Gallart *et al.*, 2020).

Consistent with this behaviour, F_{yw} was found in several studies to increase during wetter years (Bansah & Ali, 2019; Clow, Mast & Sickman, 2018; Remondi, Botter, Burlando & Fatichi, 2019; Wilusz, Harman & Ball, 2017; Zhang *et al.*, 2018) and to be higher in wetter catchments (von Freyberg *et al.*, 2018; Remondi *et al.*, 2017). The importance of rainfall intensity dynamics on catchment MTT or F_{yw} was also stressed by several authors (von Freyberg *et al.*, 2018; Soulsby, Piegat, Seibert & Tetzlaff, 2011; Remondi *et al.*, 2019; Wilusz *et al.*, 2017).

Furthermore, Stockinger *et al.* (2019) showed that catchment F_{yw} was not only sensitive to (long-term) annual hydro-climatic variations, but also to (short-term) weekly changes of the starting date of a sampling campaign.

1.3 How sensitive is F_{yw} to sampling rate?

Although F_{yw} may be estimated from irregularly and sparsely sampled tracer time series (Kirchner, 2016a), Stockinger *et al.* (2016) showed for the Erkensruhr catchment that F_{yw} almost halved and MTT doubled when the original daily or sub-daily data were aggregated to a weekly sampling rate. Several studies have shown that, to obtain sound estimates of hydrological dynamics, samples must be taken at the corresponding time scales (Kirchner, Feng, Neal, & Robson, 2004; von Freyberg, Studer and Kirchner, 2017; Neal *et al.*, 2012).

However, what temporal sampling resolution adequately covers (including cost efficiency) the highly variable age distribution of stream water is still to be tested (Sprenger *et al.*, 2019b).

Yet, tracer concentrations must be weighted by the corresponding precipitation and streamflow volumes for their masses to be compared (Kirchner, 2016a). Walling (1988) provided classic examples of the issues relating to both the representativeness of sediment sampling and the adequate flow-weighting of concentrations.

However, many of the F_{yw} and MTT studies are based on monthly to weekly sampling schemes constrained in their designs by operational rather than hydrological factors. Frequently, authors wonder about the representativeness of their samples, but detailed information on the flow regimes or comparisons between those sampled and those only recorded are rarely given. Hydrographs are scarce and flow duration curves are rarely discussed or shown. Mass weighting of tracer concentrations is a normal procedure in precipitation, but is seldom applied to stream waters.

1.4 Are F_{yw} values lower in mountainous catchments?

Several studies found that high-gradient or -elevation catchments have lower F_{yw} values or longer MTT (Jasechko *et al.*, 2016; Jasechko, Wassenaar & Mayer, 2017; Lutz *et al.*, 2018; Song *et al.*, 2017), whereas other studies found a converse relationship (Clow *et al.*, 2018; Zhang *et al.*, 2018) or no clear relationship (von Freyberg *et al.*, 2018; Soulsby *et al.*, 2011). Although von Freyberg *et al.* (2018) found no significant relationships between F_{yw} and the elevation gradient in their 22 studied Swiss catchments, their median value was found to be consistent with the observation of Jasechko *et al.* (2016) that young water fractions tend to be smaller in steeper landscapes. Using monthly sampled water geochemistry, Frisbee *et al.* (2011) found that groundwater contributions increased with increasing scale in mountainous drainage areas greater than 100 km², but decreased with increasing scale in headwater drainage areas smaller than 100 km². On the other hand, long-term weekly or bi-weekly stream water sampling in a high mountain 1.55 km² catchment showed a low (4.5%) contribution of groundwater to stream flow (Dwivedi *et al.*, 2018). Daily data in two small (0.51 and 3.47 Km²) mountain catchments at Plynlimon (Wales) showed that MTTs were as short as 0.36 and 0.82 years, respectively (Kirchner *et al.*, 2001). However, simulation exercises made at hourly and daily time scales showed higher F_{yw} and shorter MTT values in steeper catchments, regardless of the climate (Remondi *et al.*, 2019).

Although there is no consensus, the hypothesis with most support, though it runs contrary to intuition, is that mountain catchments tend to yield lower F_{yw} and longer MTT, attributed to the deeper infiltration of rain water (Jasechko *et al.*, 2016). However, as mountainous catchments are commonly considered to have fast hydrological responses to precipitation (Arnell, 1989), the question arises whether mountain catchments have always been sampled at a temporal frequency appropriate to their hydrological dynamics for assessing sound F_{yw} values.

This paper aims to address the research gaps outlined by applying the recent F_{yw} developments to investigation of the turnover of waters in diverse hydrological compartments of the small Can Vila research catchment (Vallcebre Research Catchments; Gallart, Llorens, Latron & Regüés, 2002; Llorens *et al.*, 2018). Our work contributes to the methodological development and understanding of F_{yw} by testing its application through weekly to sub-hourly precipitation and stream water samples along with fortnightly mobile soil and shallow ground water samples. Further, our work aims to shed light on the interpretation of F_{yw} by combining results with the understanding of hydrological processes in a long-term research catchment. Thus, the objectives of this research are both to improve understanding of the hydrological functioning of the Can Vila catchment and to test the F_{yw} concept in an intensively investigated Mediterranean mountain environment.

2. Materials and Methods

2.1 Study area

The study was conducted in the Can Vila catchment (0.56 Km²), one of the sub-catchments of the Vallcebre research catchments (Llorens *et al.*, 2018) at the headwaters of the Llobregat River, about 130 km north-east of Barcelona, on the southern margin of the Pyrenees, Catalonia (42°12' N, 1°49' E).

In the Can Vila catchment, elevations range between 1,115 and 1,458 m above sea level. Slope gradients are moderate, with a mean value of 25.6% (Latron & Gallart, 2007), and have dominant north-east aspects. Before and during the 19th century, most of the hillslopes were deforested and terraced for agricultural purposes. The terraces are mostly 10 to 20 meters

wide and limited by a stone wall up to 2 meters high, covering around half the area. Along with terraces, a network of artificial ditches was also built in order to prevent soil saturation and to convey surface runoff (Llorens, Latron & Gallart, 1992; Gallart, Llorens & Latron, 1994). Following land abandonment during the second half of the 20th century, spontaneous forestation by *Pinus sylvestris* patches occurred (Poyatos, Latron & Llorens, 2003) and forest now covers 34% of the catchment. The remainder of the catchment is covered by pasture and meadows. The main channel is 1 to 2 m wide and is not deeply incised near the outlet.

The bedrock of the Can Vila catchment consists almost entirely of smectite-rich mudrocks with sandstone and gypsum layers of the continental Tremp formation (Upper Cretaceous-Palaeocene), with the exception of the western part, where lacustrine micritic limestone appears almost vertically. This catchment is considered to be totally watertight, with no noticeable deep percolation due to the underlying clayey bedrock (Latron, Soler, Llorens & Gallart, 2008), although some local aquifers occur in sandstone and gypsum layers that feed small permanent sources within the catchment. Soils developed over mudrocks are predominantly of silt-loam texture. Topsoil is rich in organic matter (on average 4.1% from 0 to 55 cm below the ground surface) and well-structured, with high infiltration capacity in the upper 20 cm (Solé, Gallart, Pardini & Aringhieri, 1992), while hydraulic conductivity decreases rapidly at greater depth (Rubio, Llorens & Gallart, 2008). These soil conditions result in formation of shallow permanent aquifers over the impervious bedrock and some transient perched aquifers during major rainfall events. Soil water content is characterized by periods of marked deficit in summer and, though less pronounced, in winter. In summer, soil cracking occurs, which enhances infiltration capacity. Soil thickness varies greatly as a consequence of terracing, ranging from less than 50 cm in the inner part of terraces to more than 3 m in their outer part (Latron *et al.*, 2008). A small part of the catchment (0.9%) is occupied by bare limestone and mudrock outcrops with little-developed badland landforms.

The climate is defined as Mediterranean sub-humid, with a marked water deficit in summer. Long-term (1988-2013) mean annual precipitation is 880 ± 200 mm (Llorens *et al.*, 2018), with on average 90 rainy days per year (Latron, Llorens & Gallart, 2009). Snowfall accounts for less than 5% in volume. The rainiest seasons are autumn and spring with over 100 mm/month in October, November and May (Latron & Gallart, 2008). Winter is the season with least rainfall, while in summer convective storms may produce significant rainfall inputs. The mean annual temperature is 9.1°C at 1,260 m a.s.l. and mean potential

evapotranspiration, calculated as proposed by Hargreaves and Samani (1982), is 823 ± 26 mm/year. The isotopic signatures of meteoric water in Vallcebre are influenced by Western Mediterranean and Atlantic Ocean air masses and their weighted averages between 2011 and 2016 were $-44.14 \pm 2.30\text{‰}$ ($\delta^2\text{H}$), $-7.17 \pm 0.29\text{‰}$ ($\delta^{18}\text{O}$) and $13.19 \pm 0.51\text{‰}$ (d-excess), after Casellas *et al.* (2019).

The combined dynamics of rainfall and evapotranspiration result in dry and very dry periods in winter and summer, respectively, whereas wet periods occur in spring and late autumn (Latron & Gallart, 2007). Three types of runoff events were identified on the basis of hydrometric observations (Latron & Gallart, 2007; 2008). Intense rainfall events during summer induce flash floods with very low runoff coefficients, attributed to infiltration-excess overland flow on bare bedrock and badland areas. Second, during transitions from dry to wet conditions, more frequent and/or greater rainfall events induce larger runoff events with moderate runoff coefficients with long response times and relatively gentle recessions, attributed to a scattered pattern of perched soil saturation. Third, under wet conditions, moderate rainfall events induce large and lasting runoff events associated with rapid responses of the water table, attributed to overland flow on saturated areas and return flow. Flow in the Can Vila stream usually ceases each year for a few weeks during the summer, though these interruptions do not mean a break in the continuity of subsurface waters, as shown by the fact that remaining pools in the stream bed rarely dry out. Furthermore, the use of tritium to investigate the turnover of waters during low-flow conditions (Gallart *et al.*, 2016) revealed MTTs of nearly 5 years for shallow open groundwaters and 7.5 years for both stream base flow and a permanent spring near the centre of the catchment.

Two-component hydrograph separation studies using stable isotopes indicate that pre-event water contributed between 30% and almost 100% to total runoff, depending on antecedent moisture conditions, the extent of saturated areas within the catchment and precipitation characteristics (Latron, Roig-Planasdemunt, Llorens & Gallart, 2015; Cayuela *et al.*, 2019). During low to moderate-intensity rainfall events (winter, spring, autumn), pre-event water contribution was dominant (>90%). Conversely, during high-intensity summer storms, pre-event water contribution was lower (30% to 50%) and the response corresponded mostly to new water. Pre-event water contribution at the event scale decreases with increasing maximum rainfall intensity. In addition, pre-event water contribution and the maximum

suspended sediment concentration observed at the outlet correlate negatively, which supports that summer floods are mainly caused by infiltration excess runoff generated on badlands and degraded areas of the catchment (Latron *et al.*, 2015).

2.2 Data acquisition

2.2.1 Hydrological measurements and water sampling

Rainfall volumes for the period 2011-2017 were recorded at 5-minute steps with a tipping-bucket rain gauge near the gauging station (Figure 1).

The depths to the water table at the VP01 and VP05 piezometers were recorded every 20 min with autonomous Micro-Diver sensors (Van Essen Instruments), subsequently corrected for atmospheric pressure changes.

Stream discharge was measured at the Can Vila gauging station, by means of a 90° V-notch weir with a water pressure sensor (6542C-C, Unidata) connected to a data-logger (DT50, Data Taker). Mean water level values were recorded every 5 minutes and converted to discharge values with an established rating curve calibrated with manual discharge measurements (Latron & Gallart, 2008). Discharge values were originally expressed in L s^{-1} and converted, without time aggregation, into millimetres per day (mm d^{-1}) for comparison with other studies.

In the Can Vila catchment, waters for stable isotope ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) analyses were sampled from rain and stream at one site at the catchment outlet, from groundwater at two sites (VP01 and VP05) and from mobile soil water at two sites (VL01 and VL02) (see Figure 1).

Rainfall samples for isotope analysis were taken from May 2011 to July 2013 and from May 2015 to November 2017. Two types of rain water samplers were used. A bulk rainfall sampler, consisting of a 180-mm diameter funnel connected to a 1 L plastic bottle with a pipe with a loop, provided information of the isotopic composition of rainfall on an approximately weekly basis. Rain water was further sampled automatically at 5 mm rainfall intervals with a sequential rainfall sampler, using an open collector (340 mm diameter) connected to an automatic water sampler (24 500-mL bottles, ISCO 2900). Both containers (bottle and sampler) were buried in the ground to avoid evaporation. The two sampling

records were aggregated (i.e., using the shortest time interval available and removing duplicate samples), providing a data set of 464 rainfall isotopes samples.

As shown by Cayuela *et al.* (2019), the location of the rainfall sampling site at the lowest part of the Can Vila catchment means that the sampled isotope signature is more enriched than the average for the catchment. However, the isotopic enrichment of throughfall in the forested areas compensates for this effect. Consequently, no compensation of the isotopic signature in precipitation due to elevation effects was deemed necessary.

Soil mobile waters were sampled at two locations with a battery of low-suction cup lysimeters installed between 50 (2 lysimeters) and 100 (4 lysimeters) cm depth. The soil water sample at each location was a mixture of the water collected at different lysimeters and depths. Soil water was sampled weekly or fortnightly from May 2011 to July 2013 when water could be extracted. Over the study period, 63 samples from VL01 and 37 from VL02 were analysed for isotopic composition.

Groundwaters were sampled at two locations near the surface of the water table with a manual peristaltic pump, as electrical conductivity profiles conducted on several occasions showed no stratification of the waters. VP01 is a 2.06 m-deep piezometer lined with a 55 mm-diameter PVC tube, which is sealed in the upper 0.5 m to prevent entrance of surface waters and has open access below. VP05 is a 4.22 m-deep abandoned well. Its walls are covered by boulders, allowing water to flow throughout the full depth. Groundwater was sampled weekly or fortnightly from May 2011 to July 2013. A total of 36 samples were taken from the VP01 piezometer (that sometimes dried out) and 71 from the (permanent) VP05 well.

Stream water was sampled from May 2011 to September 2013 and from late May 2015 to May 2016, using a sampling scheme designed for obtaining information for isotopic hydrograph separation (IHS) at the event scale (Cayuela *et al.*, 2019). Manual grab samples were taken weekly during visits and two automatic water samplers (24 1 L bottles, ISCO 2700) were operated by the data-logger. One sampler was scheduled to take a sample every 12 hours and the other was triggered when stream water level exceeded a certain threshold, taking samples at a higher rate when the water level rose than when it declined. In total, 858 stream samples were analysed for their isotopic composition. The final sampling rate was

between 30 minutes and 1 week, although there are some gaps due to the drying of the stream.

2.2.2 Isotopic analyses and pre-treatment

During the sampling periods, all samples were collected once a week during field visits. Manual samples of stream, soil and groundwaters were directly collected in glass vials. The bottles of the automatic rainfall and stream samplers were capped and transported to the laboratory under cold conditions, where two samples from every bottle were deposited in 3-ml glass vials. These vials were fully filled to avoid bubbles and sealed with plastic paraffin film to avoid fractionation caused by evaporation. For each sample, a replica was prepared. All samples were stored at 3-4°C prior to analysis.

Stable isotopes of water (^{18}O and ^2H) were analysed by a Cavity Ring-Down Spectroscopy Picarro L2120-i isotopic water analyser at the Scientific and Technological Services of the University of Lleida. All isotope data were expressed in terms of δ -notation as parts per mille (‰) and calibrated to Vienna Standard Mean Ocean Water (V-SMOW) (Craig, 1961). Accuracy of the analyses, based on the repeated analysis of four reference water samples, was $< 0.1\text{‰}$ and $< 0.4\text{‰}$ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. When samples contained organic compounds, a post-processing correction was applied (Martín-Gómez *et al.*, 2015).

The isotopic signatures of the precipitation samples were weighted by their corresponding precipitation depths before further calculations. Furthermore, following common procedures (*e.g.* McGuire & McDonnell, 2006; Jasechko *et al.*, 2014; Lutz *et al.*, 2018), a soil water-balance model was used to estimate the effective precipitation for weighting the isotopic signature of the waters entering the hydrological system, under the hypothesis that precipitation in the warmer months evaporates more and contributes less to the hydrological compartments than precipitation in the remaining months. For this purpose, the conceptual lumped Thornthwaite-Mather model (Steenhuis & van der Molen, 1986) was implemented at a weekly time step, after calibration with the flow records of the Can Vila catchment. Then, the convenience of filtering the input precipitation signal with an effective precipitation model was evaluated using two approaches, based on the comparison of mass balances of stable water isotopes between seasons; the first proposed by Grabczak *et al.* (1984) and Maloszewski *et al.* (1992) and the second by Kirchner and Allen (2020). The

methods and results of the effective precipitation model and the corresponding tests are described in detail in the Supporting Information.

As both the isotope ratio of groundwater and its temporal variability varied with the water table level at VP05, two different approaches were adopted. First, the available record was divided into two sub-series: samples taken when the water table level was deeper than 2.25 m were classified in the ‘deep’ group; and samples from shallower water levels, in the ‘shallow’ group. Second, an attempt was made to obtain a mass-averaged isotope ratio by weighting with the exponent of the water table level over its minimum value, used as a surrogate of groundwater flow (Latron & Gallart, 2008).

Stream water samples were taken at different frequencies and discharge regimes. Therefore, their isotopic signatures were flow-weighted to obtain mass-representative values (Kirchner, 2016a) and time-weighted for comparison with other studies (Jasechko *et al.*, 2016; von Freyberg *et al.*, 2018). In addition, following the methods proposed by Kirchner (2016b) and von Freyberg *et al.* (2018), the original record was divided into a set of sub-samples according to the respective discharge rates, in order to analyse the dependence of the young water fraction on the flow regime. Finally, for comparison with other studies that used weekly to monthly sampling rates, a subordinate sample set with a weekly rate was extracted from the original one.

2.3 Young water fraction estimations

Following the methods and notations proposed by Kirchner (2016a), the seasonal amplitudes A and phases φ of the $\delta^{18}\text{O}$ signatures c of waters in precipitation, estimated recharge, stream, soil and groundwater in the catchment were calculated by (weighted as appropriate) non-linear fitting through the equation:

$$c = A \sin(2 \pi f t - \varphi) + k \quad (1)$$

where f (year^{-1}) is the frequency of the cycle ($f=1$ for a seasonal cycle), t is time (years with decimal fractions) and k is the zero value or vertical shift of the sinusoid. In young water fraction studies, non-linear fitting methods that limit the influence of outliers are commonly used (*e.g.*, Kirchner, 2016a; Stockinger *et al.*, 2016; von Freyberg *et al.*, 2018). In our case, the distribution of $\delta^{18}\text{O}$ in precipitation had less extreme values than normal distribution (platykurtic, kurtosis $K = 1.0$); whereas in the stream water $\delta^{18}\text{O}$ distribution, the extreme

values were much more important (leptokurtic, $K = 26.9$). Therefore, we decided to use least-squares fitting, as the outliers might contain hydrologically relevant information.

Subsequently, the F_{yw} for the waters investigated (i.e., stream water, groundwater, mobile soil water) was estimated as the ratio between the amplitudes of the isotope ratios in these waters and the amplitude of precipitation (or recharge) waters (Kirchner, 2016a):

$$F_{yw} = A_s/A_p \quad (2)$$

where the p and s subscripts represent precipitation and investigated waters, respectively.

Following the notation used by von Freyberg *et al.* (2018), we designated F_{yw} as the time-weighted young water fraction and F_{yw}^* as the flow-weighted young water fraction.

Although the TTD of waters was not an objective of this study, research into the young water fractions for a set of hydrological compartments and stream flow regimes cast doubt on the potential role of the threshold age τ_{yw} of these fractions. For this purpose, the shape parameter α of the likely gamma distribution for every compartment and stream flow regime sub-samples was estimated by iteratively solving the implicit equation (Kirchner, 2016a):

$$\varphi_s - \varphi_p = \alpha \left(\sqrt{(A_s/A_p)^{-2/\alpha} - 1} \right) \quad (3)$$

where the subscripts s and p correspond to the stream and precipitation, respectively, and A and φ represent sinusoid amplitudes and phase shifts, respectively. Once the shape parameter α was obtained, the corresponding threshold ages τ_{yw} of the young water fractions were calculated by means of the following second-order polynomial fit (Kirchner, 2016a):

$$\tau_{yw}/T \approx 0.0949 + 0.1065 \alpha - 0.0126 \alpha^2 \quad (4)$$

Finally, the dependence of the young water fraction on stream discharge or its discharge sensitivity was investigated by two methods. First, we calculated F_{yw} for different quantiles of the flow regime (similar to Figure 7 in von Freyberg *et al.*, 2018). Second, we assumed that F_{yw} was not a fixed value but that it increased with discharge up to a limit value of 1, following an exponential-type equation (Gallart *et al.*, 2020):

$$F_{yw}(Q) = 1 - (1 - F_0) \exp(-Q S_d) \quad (5)$$

where F_0 (1) is the Y-intercept or virtual F_{yw} for $Q=0$ and S_d (unit of Q^{-1}) is the discharge sensitivity metric. These metrics can be obtained by non-linear fitting of the equation (Gallart *et al.*, 2020):

$$c_s(t) = A_p[1 - (1 - F_0) \exp(-Q(t) S_d)] \sin(2 \pi f t - \varphi_s) + k_s \quad (6)$$

where subscripts s and p are the same as in Eq. (2).

In a first exercise, F_{yw} and its discharge sensitivity were investigated in stream waters by applying Eqs. (1), (2) and (6) to the full record available, lumping together the 58 months as in a single year. In a subsequent step, these equations were used on several 12-month time windows of both precipitation and stream waters, in order to investigate the relevance of the precipitation forcing.

Finally, although the 858 water samples/discharge values taken at variable time steps could be expected to provide a reasonable picture of the stream dynamics at Can Vila, a further test was conducted by applying Eq. (5) to the 228,095 5-minute discharge readings available for the sampling periods. The flow-averaging of the resulting $F_{yw}(Q)$ simulations for all these readings provided a hypothetically fully-sampled flow-weighted young water fraction that we labelled F_{yw}^{**} .

The SPSS (IBM Corp.) statistical package, including a Levenberg-Marquardt algorithm for non-linear estimations, was used. Uncertainties were mostly expressed as standard errors except for the threshold ages τ_{yw} , where the uncertainties were expressed as 90% confidence limits, using 10,000 Monte Carlo solutions of Eq. (3). Error propagation was estimated by Gaussian methods, following the guidelines of Kirchner & Allen (2020, supplement) for end-member mixing and splitting in particular, as well as calculation of weighted averages. Statistical significance was set at $p < 0.01$ and marginal significance was set at $p < 0.05$, although the probability of the null hypothesis is sometimes indicated. The notation (1) after a variable name indicates that this variable is a dimensionless number.

3. Results

3.1 Isotopic characteristics of the sampled waters

During the study period, annual precipitation was similar to the long-term mean value (860 mm/year), with a 12-month minimum of 671 and maximum of 996 mm/year. A total of 3,902 mm of precipitation was measured and 464 samples were taken during the whole period. The isotope ratios of precipitation samples show a clear seasonal variation (Figure 2), more marked for the isotope ratios weighted with the gross precipitation than for those weighted with the effective recharge simulated with the Thornthwaite-Mather model.

Similarly, seasonal variations are seen in the isotope ratios of mobile soil water (upper panel in Figure 3) and, to a much lesser extent, in groundwater samples (lower panel in Figure 3). At VP05 (but not at VP01), the scatter of groundwater $\delta^{18}\text{O}$ values was related to the dynamics of the water table (Figure 4 and Table 1): when the water table rose, the values tended to vary more, with the isotope ratios ranging from the minimum to the maximum recorded for the time period studied. However, when the water table was at its lowest (-3.5 m), the isotope ratios tended to be less variable.

Total stream discharge was 1,014 mm, but it behaved differently in the two sampling periods (Figure 5). During the first one, there was a succession of wet and dry episodes, with several interludes without any runoff. The second period was wetter (annual precipitation = 996 mm), with sequences of intermediate events and the highest 5-minute discharge measured during the entire record ($2.619 \text{ m}^3\text{s}^{-1}$, equivalent to 404 mm d^{-1}).

The overall results of the ^{18}O analyses in the compartments studied are synthesized in Table 1. Mean simulated recharge was more depleted in heavy isotopes than precipitation was, because the simulated soil water balance is more adverse in summer and, in consequence, the recharge weights of summer-enriched isotopic sample signatures were usually lower than those in the colder seasons.

Some other differences between inputs and compartments are given in Table 2. The isotope ratios of precipitation were slightly more depleted than in any other compartment except for flow-weighted stream waters, although the only marginally significant differences were with groundwater at VP01 and deep groundwater at VP05. The isotope ratios for simulated recharge were even more depleted than for precipitation, but otherwise nearly all the

differences between recharge and catchment compartments were either significant (soil waters and groundwaters at VP01) or marginally significant (groundwaters and time-weighted stream waters).

The volume-weighted ^{18}O and ^2H values of the precipitation waters drew a Local Meteoric Water Line (LMWL) with an adjusted determination coefficient $R^2=0.961$ ($p<0.001$):

$$\delta ^2H = 7.96 \delta ^{18}O + 13.3 \quad (7)$$

The sampled soil waters plotted reasonably close to the LMWL (Figure 6), although some of the more enriched samples taken at VL01 were slightly below the line, suggesting kinetic fractionation due to evaporation. Stream water samples plotted close to the LMWL, with the exception of the few most depleted samples, which corresponded to a runoff event on 5 April 2016, that were clearly located below the LMWL, following the same trend as the precipitation waters during this event (further information on precipitation isotopy at Can Vila can be found in Casellas *et al.*, 2019). Groundwaters showed no relevant displacement from the LMWL (not shown).

3.2 Assessing young water fractions

We tested using both the gross precipitation and the net precipitation obtained with the recharge model, for weighting the precipitation samples. The results, shown in Table 2, revealed that the isotope ratio of the simulated recharge (or effective rainfall) was more depleted than all the other hydrological compartments. This was, therefore, discarded from the following analysis. On the contrary, as the isotope ratio of gross precipitation was similar to the diverse compartments, it can be considered appropriate as input signature. The validity of this option was subsequently tested by means of the mass balance methods reported in the Supporting Information, which confirmed that summer precipitation contributed in a similar way to the diverse hydrological compartments as precipitation in the rest of the year did.

Given these converging indicators, the precipitation-weighted isotope ratios were used for subsequent analysis of the seasonal variations, although the recharge-weighted signature was studied and reserved for some comparisons. The resulting implications are reviewed in the Discussion section.

The sine-wave fitting with Eq. (1) was subsequently applied to the isotope ratios of all these eleven compartments: mass-weighted precipitation (i), mass-weighted simulated recharge (ii), mobile soil water at VL01 (iii) and VL02 (iv), groundwater at VP01 (v) and VP05 (vi), level-weighted groundwater at VP05 (vii), groundwater at VP05 when the water table was shallow (0 to 2.25 m deep) (viii) and deep (deeper than 2.25 m) (ix), time-weighted stream water (x) and flow-weighted stream water (xi). In a further step, Eq. (1) was also applied to both time-weighted and flow-weighted stream water samples taken at a weekly rate.

The results show a wide range of amplitudes and young water fractions, as calculated with Eq. (2) using precipitation A as A_p (Table 3). Attending to the resulting sinusoid amplitudes and F_{yw} obtained, these eleven hydrological compartments can be arranged with high statistical significance ($p < 0.001$, F-test) in four main groups: 1) mobile soil waters, flow-weighted stream water and shallow groundwater at VP05 had the highest F_{yw} and F_{yw}^* (0.207 to 0.344). 2) Level-weighted groundwater at VP05 had an intermediate F_{yw} (0.115). 3) Time-weighted stream water and bulk groundwater at VP05 had low but identifiable F_{yw} (0.062 to 0.078). 4) Finally, groundwater at VP01 and deep groundwater at VP05 had F_{yw} not significantly different from 0. This arrangement demonstrates a good relationship between flow-weighted stream F_{yw}^* and the more dynamic compartments of the catchment, clearly separated from the much lower rank of time-weighted stream F_{yw} and groundwaters.

3.3 Assessing the discharge sensitivity of the young water fractions

For the Can Vila catchment, the flow-weighted young water fraction ($F_{yw}^* = 0.226 \pm 0.028$) was higher than the time-weighted young water fraction ($F_{yw} = 0.062 \pm 0.008$), suggesting a clear dependence of the young water fraction on discharge. To analyse this dependence, the time-weighted young water fractions for different quantiles of the flow regime were analysed as shown in Figure 7 (similar to Figure 7 in von Freyberg *et al.*, 2018), adapting the range to portray the highest sampled flows (those exceeded 0.25% of time and 16.6% of flow). This figure shows that F_{yw} increased with increasing discharge, from nearly 0 at the lowest discharge to nearly 1 for $Q \geq 24 \text{ mm d}^{-1}$, and underlines the usefulness of Eq. (5). This equation provides a basal (virtual for zero discharge) young water fraction that is indistinguishable from 0 ($F_0 = 0.024 \pm 0.028$) and rather large exponential sensitivity ($S_d = 0.056 \pm 0.01 \text{ d mm}^{-1}$) parameters.

The wide range of F_{yw} values observed for the diverse compartments and stream flow quantiles might cast doubt on the potential role of the threshold age τ_{yw} that defines these fractions in the results. To analyse this question, Figure 8 shows the comparison of these time thresholds obtained from Eqs. (3) and (4). This graph demonstrates that the thresholds did not play any role because they were consistently similar for the diverse compartments and stream flow quantiles analysed, although the uncertainty towards higher values strongly increased with increasing F_{yw} .

3.4 Analysing different sampling periods: role of precipitation forcing

The Can Vila catchment data used in this research cover one period of over two years and another of one year. To analyse the variation of F_{yw}^* and S_d under different precipitation conditions, five 12-month time windows of both precipitation and stream waters were selected from the first period and compared with the last one-year period and the full record, as shown in the upper graph of Figure 9. Although both F_{yw}^* and S_d roughly increased with annual precipitation (upper graph), with the wettest year (996 mm) having the highest F_{yw}^* (0.34) and S_d (0.147 d mm⁻¹), the trend is highly irregular. Indeed, the driest year (671 mm) shows an intermediate F_{yw}^* (0.16) with a quite low S_d (0.011 d mm⁻¹), while the second wettest year (972 mm) shows a lower F_{yw}^* (0.12) but a higher S_d (0.035 d mm⁻¹).

When the coefficient of variation of discharge was used instead of precipitation as the forcing variable (lower graph in Figure 9), two very distinct conditions were shown: periods with a low coefficient of variation of discharge had moderate F_{yw}^* values and low S_d values, whereas the period with a high coefficient of variation had high values for both metrics.

3.5 Role of sampling rate

All the results shown above for stream waters are based on the dynamic sampling design described in the Methods section. Nevertheless, most published F_{yw} studies are based on weekly to monthly sampling frequencies. As many authors agree that stream waters' transit time and F_{yw} results are affected by sampling rates, we used weekly spaced samples to calculate the main metrics describing F_{yw} and subsequently compared these results with the dynamic sampling results shown above.

The results show that both time-weighted and flow-weighted young water fractions using a weekly sampling frequency ($F_{yw} = 0.044 \pm 0.014$ and $F_{yw}^* = 0.103 \pm 0.033$) were significantly lower than results with dynamic sampling (Table 4).

Furthermore, the highest discharge sampled at Can Vila was 226 mm d^{-1} , a little more than half the maximum discharge recorded during the same period (404 mm d^{-1}). Therefore, as we know that F_{yw} approaching 1 are associated with the highest flows, the question arises as to whether the dynamic sampling implemented at Can Vila was sufficient to capture the real behaviour of F_{yw} dynamics. For this purpose, Eq. (5) was applied to simulate the $F_{yw}(Q)$ for every 5-minute discharge reading available for Can Vila during the sampling period and these simulated young water fractions were weighted with the corresponding discharge readings. The resulting flow-weighted young water fraction, as a measurement of the virtually perfect sampling that we name F_{yw}^{**} , was 0.304 ± 0.030 . The differences between the metrics obtained with the different sampling strategies and weighting are shown in Table 4, demonstrating that, if F_{yw}^{**} is taken as the unbiased young water fraction, the F_{yw}^* estimates obtained with the dynamic and weekly sampling were underestimated by 25% and 66%, respectively.

In order to obtain a graphic comparison of the behaviour of the different sampling methods, the 5-minute flow record was ordered from high to low discharges, and the corresponding time, flow and F_{yw}^* were accumulated for the 5-minute record and flow for the two sampling designs (Figure 10). This compared the accumulated time (time-exceedance) of every record with the corresponding flow exceedance and young water fraction exceedance, making it easier to understand the results shown in Table 4. Both the accumulated 5-minute flow and F_{yw}^* curves start close to 0 exceedance, showing that the highest recorded flows, in spite of their high value and F_{yw} being close to 1, occurred so rarely that the exceeded values for flow and F_{yw} are not relevant, which makes clear that the 5-minute record does indeed represent a thorough virtual sampling.

The highest discharges associated with the samples taken with the dynamic design exceeded 0.01% of time and represent 2.7% of flow and about 25% of the young water fraction (when a sufficient number of samples were taken for estimating F_{yw}^*). This means that about 25% of the young water fraction was missed for the assessment by the dynamic sampling design because this amount was associated with the higher discharges that were not sampled. Finally, the highest discharges associated with the samples taken with the weekly sampling

rate are exceeded 0.6% of time and are associated with 17% of flow and about 66% of the young water fraction, which was also lost for the assessment.

4. Discussion

Our results show behaviour of young water fractions at the Can Vila catchment that is much more dynamic than that reported in any other catchment. The identification of this behaviour is attributable to the Mediterranean climate setting, the small size of the catchment and the high sampling frequency available at this site for stream water tracer data.

An early outcome of this research was the need for an updated design of the discharge sensitivity of the young water fraction, adequate to cope with the non-linear behaviour of F_{yw} with discharge, as shown in Figure 7. This question was resolved previously, leading to the development of Eqs. (5) and (6), as described in Gallart *et al.* (2020).

Other results help to improve the conceptualisation of the hydrological functioning of the Can Vila catchment and to review questions raised by other researchers in this field, as detailed in the introduction: the fate of rain water fallen in summer, the dependence of the young water fraction on precipitation forcing, the effect of sampling frequency on catchment water turnover investigations and the young water fractions delivered by mountain catchments.

4.1 The recharge assumption

An unexpected result of this study was the finding that the isotopic signature of gross precipitation was adequate for analysing the turnover of surface and shallow groundwaters in the Vallcebre catchments, without any need for reducing the isotopic contribution of summer precipitation. In this catchment, summer is a period when evaporative demand is usually much higher than precipitation (as shown in Table S1 in the Supporting Information); flow in the streams strongly decreases and ceases in several reaches, saturated areas disappear and both soil water content and water table level decrease (Llorens *et al.*, 2018). Nevertheless, our results with Eqs (S2), (S3) and (S4) in the Supporting Information indicate that summer precipitation does not rapidly evaporate and does not evapotranspire more than precipitation during the rest of the year, but it contributes in a similar way to the

diverse hydrological compartments. Therefore, most of the water intensely evapotranspired in summer appears to be previously stored soil water.

A study by Sprenger *et al.* (2019a) carried out during the second period analysed (2015) in a forested plot within the Can Vila catchment showed that mobile soil water was consistently more enriched in heavy isotopes than ground and stream waters, a result analogous to ours in Table 2. However, water held in smaller soil pores and potentially used for transpiration by vegetation remained more depleted than any other compartment and was mainly refilled during winter. Our results in Table S1 of the Supporting Information show that 1,239 mm of evapotranspired water was sustained from precipitation between September and May, whereas only 475 mm was sustained from precipitation between June and August, in convergence with the findings of Sprenger *et al.* (2019a), but at the catchment scale.

Such findings had an impact on F_{yw} estimates in the diverse compartments studied. A hypothetical decreased contribution of summer precipitation would not only cause a shift in the mean input isotopic signature but also a reduction of its seasonal amplitude and, subsequently, an increase in the young water fractions. Figure 7 demonstrates that the young water fractions estimated at Can Vila for the highest flows are around 1, the maximum possible value. However, when the isotopic signature of the simulated recharge is used instead of that of the precipitation as A_p in Eq (2), the five points in Figure 7 that correspond to the highest flow regimes take excessive F_{yw} values with a mean of 1.30, although the excess does not reach statistical significance ($p=0.105$).

4.2 The role of precipitation forcing

As the young water fraction usually increases with discharge, wetter years and wetter catchments may be expected to deliver higher young water fractions than dry ones, as found by several authors (Bansah & Ali, 2019; Clow *et al.*, 2018; Remondi *et al.*, 2019; von Freyberg *et al.*, 2018; Wilusz *et al.*, 2017; Zhang *et al.*, 2018). However, our results shown in Figure 9 make clear that annual precipitation is an insufficient driver for the behaviour of F_{yw}^* at Vallcebre, whereas the variation of discharge might better explain F_{yw}^* and particularly S_d . These results are consistent with those obtained by other authors on the role of temporal patterns or rainfall depths and intensities (von Freyberg *et al.*, 2018; Soulsby *et al.*, 2011; Wilusz *et al.*, 2017), and particularly with the modelling exercise of Remondi *et al.* (2019), which suggested that catchments in semi-arid and Mediterranean climates have not only

lower but also more variable young water fractions than catchments in more humid climates.

This result recalls the complexity of the runoff generation mechanisms at Can Vila already investigated by hydrometric and tracing methods and shows the need for further analyses at the event scale by combining the study of young water fractions with other event characteristics such as rainfall depth and intensity, antecedent conditions and new water contribution. This would contribute to investigating not only how the catchment behaves but also which processes lead to this behaviour (Kirchner, 2019).

Yet, our results also support doubt on the validity of single one-year F_{yw} investigations for characterizing catchment behaviour (Stockinger *et al.*, 2019) and underline that both MTT and F_{yw} depend on meteorological forcing at an extent that may mask physiographic catchment characteristics (von Freyberg *et al.*, 2018; Hrachowitz *et al.*, 2009; Kirchner, 2019; Tetzlaff, Malcom & Soulsby, 2007; Remondi *et al.*, 2019).

As with other catchment characteristics driven by climate (*e.g.*, precipitation, potential evapotranspiration, discharge), F_{yw} and its discharge sensitivity should, therefore, be compared between catchments through their long-term annual means and inter-annual variabilities.

4.3 The issue of sampling rate

The differences obtained for F_{yw} depending on the sampling rates confirm the warnings of several authors cited in the Introduction and particularly the results obtained by Stockinger *et al.* (2016). Another relevant aspect is the inadequacy of the time-weighted young water fraction in a catchment with such variant discharge as Can Vila, even with the intensive sampling design implemented for this study.

This exercise shows that even an intensive sampling design like the one for Can Vila may underestimate F_{yw}^* if it is sensitive to discharge and if flow rates have a high variability, because a relevant part of the young water fraction is associated with the higher, unsampled discharges. The method applied in Section 3.5 may be used to estimate the young water fraction F_{yw}^{**} that could be measured with a thorough sampling design, *e.g.* one with continuous *in-situ* measurements.

Therefore, investigations of the catchment F_{yw} should analyse the flow duration curves, if detailed flow records are available. The relevant evaluating variable in this analysis is not the time exceedance of discharge values, but their flow exceedance, i.e. the fraction of flow associated with the higher discharges. Furthermore, if the S_d discharge sensitivity of F_{yw} has been investigated, F_{yw}^{**} can then be assessed to evaluate the quality of the metric obtained and to ponder the possible advantage of implementing a more detailed sampling design. Unfortunately, the weekly sampling performed at Can Vila is inadequate for this purpose, because the very low value of S_d obtained with this design greatly underestimates F_{yw}^{**} .

4.4 Young water fractions delivered by mountainous catchments

With a mean topographic gradient of 25.6%, the F_{yw} predicted for Can Vila by the overall assessment of Jasechko *et al.* (2016) would be about 0.091, with 90% confidence intervals about ± 0.061 . This prediction range is fully adequate for the F_{yw} estimated at Can Vila when a weekly sampling rate is used (Table 4), with the flow-weighted estimate (0.103 ± 0.033) better adjusted than the time-weighted one (0.044 ± 0.014). Yet, when dynamic sampling is used, the time-weighted F_{yw} obtained at Can Vila (0.062 ± 0.008) also falls well within the range of the global analysis of Jasechko *et al.* (2016).

Nevertheless, the flow-weighted F_{yw}^* estimate obtained at Can Vila with dynamic sampling (0.226 ± 0.028) is not in line with the overall relationship between topographic gradient and F_{yw} of Jasechko *et al.* (2016), while it is very close to the median (0.21) and a little lower than the mean (0.26) of the F_{yw} obtained by these authors for the full sample of 254 rivers. Furthermore, the fully-sampled flow-weighted young water fraction F_{yw}^{**} estimated at Can Vila is 0.304 ± 0.030 , a value that falls between the means obtained without weighting (0.26, 254 rivers) and with the flow-weighting (0.34, 190 rivers) of Jasechko *et al.* (2016).

These comparisons emphasize the importance of adequate sampling designs and weighting methods when catchments of diverse flow characteristics are compared. The results obtained at Can Vila demonstrate that when the variability of flow rate is high, low-frequency sampling and time-weighting designs will result in clearly underestimated young water fractions. It is not imprudent to speculate that mountainous catchments have, on average, flow rates that are more variable than those in flat areas with a similar catchment area (Arnell, 1989). Thus, reports of lower young water fractions in mountain catchments could result from an underestimation of young waters due to too low sampling frequencies

that miss covering the high young water fractions because of the flashy response in mountain catchments.

5 Conclusions

The application of the young water fraction approach to the Mediterranean Can Vila research catchment improved our understanding of the catchment response and shed light on some open questions. It highlighted the value of research in small catchments for the development of concepts and models.

In contradiction of the initial hypothesis, at Can Vila precipitation during summer contributes to evapotranspiration and runoff at a rate similar to that of precipitation during the rest of the year. Intense summer evapotranspiration seems to use mainly previously infiltrated soil water, while summer rainfalls contribute to all the hydrological compartments. This means that, to analyse the turnover of waters in the catchment, the isotope concentrations analysed in the precipitation waters had to be weighted with the gross precipitation depths instead of the “effective precipitation” ones.

Young water fractions and the corresponding thresholds τ_{yw} estimated in mobile soil and ground waters were consistent with those estimated for stream waters: mobile soil waters and shallow ground water had young water fractions similar to stream flow-weighted ones, whereas deep groundwaters had undetectable young water fractions.

The young water fraction is highly dynamic in the stream waters at Can Vila, varying between nearly 0 during low flows to nearly 1 during high runoff events. This dynamic is due to the combination of very high variability of discharge and a moderate discharge sensitivity of the young water fraction.

Furthermore, the young water fraction and its discharge sensitivity are highly varying catchment metrics at Can Vila when different 12-month periods are investigated. Thus, the young water fraction turns out to be a metric closely associated with the characteristics of meteorological forcing during the period studied and may therefore mask the role of physiographic catchment characteristics. If the young water fraction is used as a metric for catchment comparison, long-term means and variances should be used, as in other climate-driven traits such as annual precipitation or annual discharge.

The results confirmed that sampling frequency is highly relevant to investigations of young water fractions (and by extension to MTT). At Can Vila, the dynamic sampling design (with sampling frequency between 30 minutes and 1 week) underestimated the young water fraction by 25%, whereas weekly sampling would underestimate it by 66%. Water turnover studies should always be linked to the inspection of flow duration curves. In addition, when possible, the method used in Section 3.5 should be used to estimate the young water fraction associated with a virtual thorough sampling rate (F_{yw}^{**}). This helps to assess the quality of the metric obtained and to assess the possible advantages of implementing a more detailed sampling design for capturing high flows.

Finally, more research is needed to generalize the young water fractions of mountain catchments, preventing the potential underestimation associated with an insufficient sampling frequency of their waters.

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Data availability statement

The data that support the findings of this study are available from Jérôme Latron (jerome.latron@idaea.csic.es) upon reasonable request.

References

Allen, S. T., Jasechko, S., Berghuijs, W. R., Welker, J. M., Goldsmith, G. R., and Kirchner, J. W. (2019a): Global sinusoidal seasonality in precipitation isotopes, *Hydrology & Earth System Sciences*, 23, 3423–3436, <https://doi.org/10.5194/hess-23-3423-2019>.

- Allen, S. T., Kirchner, J. W., Braun, S., Siegwolf, R. T. W., and Goldsmith, G. R.: (2019 b). Seasonal origins of soil water used by trees, *Hydrology & Earth System Sciences*, 23, 1199–1210, <https://doi.org/10.5194/hess-23-1199-2019>.
- Arnell, N. (1989) Humid temperate sloping land, in: Falkenmark, M., & Chapman, T. (Eds.). *Comparative hydrology: An ecological approach to land and water resources*. The UNESCO Press, Paris. ISBN: 92-3-102571-6
- Benettin, P., Soulsby, C., Birkel, C., Tetzlaff, D., Botter, G., Rinaldo, A. (2017). Using SAS functions and high-resolution isotope data to unravel travel time distributions in headwater catchments. *Water Resources Research*, 1–15. <https://doi.org/10.1002/2016WR020117>.
- Bansah, S., & Ali, G. (2019). Streamwater ages in nested, seasonally cold Canadian watersheds. *Hydrological processes*, 33(4), 495-511. <https://doi.org/10.1002/hyp.13373>
- Casellas, E., Latron, J., Cayuela, C., Bech, J., Udina, M., Sola, Y., Lee, K-O. & Llorens, P. (2019). Moisture origin and characteristics of the isotopic signature of rainfall in a Mediterranean mountain catchment (Vallcebre, eastern Pyrenees). *Journal of Hydrology*, 575, 767-779. <https://doi.org/10.1016/j.jhydrol.2019.05.060>
- Cayuela, C., Latron, J., Geris, J., & Llorens, P. (2019). Spatio-temporal variability of the isotopic input signal in a partly forested catchment: Implications for hydrograph separation. *Hydrological processes*, 33(1), 36-46. <https://doi.org/10.1002/hyp.13309>
- Clow, D. W., Mast, M. A., & Sickman, J. O. (2018). Linking transit times to catchment sensitivity to atmospheric deposition of acidity and nitrogen in mountains of the western United States. *Hydrological processes*, 32(16), 2456-2470. <https://doi.org/10.1002/hyp.13183>
- Craig, H., (1961). Isotopic variations in meteoric waters. *Science* 133, 1702–1703. <https://doi.org/10.1126/science.133.3465.1702>
- Dwivedi, R., Meixner, T., McIntosh, J. C., Ferré, P. T., Eastoe, C. J., Niu, G. Y., Minor, R. L., Barron-Gafford, G. A. & Chorover, J. (2019). Hydrologic functioning of the deep critical zone and contributions to streamflow in a high-elevation catchment: Testing of multiple conceptual models. *Hydrological Processes*, 33(4), 476-494. <https://doi.org/10.1002/hyp.13363>
- von Freyberg, J., Allen, S. T., Seeger, S., Weiler, M., & Kirchner, J. W. (2018). Sensitivity of young water fractions to hydro-climatic forcing and landscape properties across 22 Swiss catchments. *Hydrol. Earth Syst. Sci*, 22, 3841-3861. <https://doi.org/10.5194/hess-22-3841-2018>
- Frisbee, M. D., Phillips, F. M., Campbell, A. R., Liu, F. & Sanchez, S. A. (2011). Streamflow generation in a large, alpine watershed in the southern Rocky Mountains of Colorado: is streamflow generation simply the aggregation of hillslope runoff responses? *Water Resources Research*, 47, W06512. <https://doi.org/10.1029/2010WR009391>
- Gallart, F., Llorens, P. & Latron, J. (1994). Studying the role of old agricultural terraces on runoff generation in a small Mediterranean mountainous basin. *Journal of Hydrology* 159(1-4), 291-303. [https://doi.org/10.1016/0022-1694\(94\)90262-3](https://doi.org/10.1016/0022-1694(94)90262-3).
- Gallart, F., Llorens, P., Latron, J., & Regüés, D. (2002). Hydrological processes and their seasonal controls in a small Mediterranean mountain catchment in the Pyrenees. *Hydrology and Earth System Sciences*, 6 (3), 527-537. <https://doi.org/10.5194/hess-6-527-2002>

- Gallart, F., von Freyberg, J., Valiente, M., Kirchner, J., Llorens, P. & Latron, J. (2020). Technical note: An improved discharge sensitivity metric for young water fractions, *Hydrology & Earth System Sciences*, 24, 1101–1107. <https://doi.org/10.5194/hess-24-1101-2020>
- Gallart, F., Roig-Planasdemunt, M., Stewart, M. K., Llorens, P., Morgenstern, U., Stichler, W., Pfister, L. & Latron, J. (2016). A GLUE-based uncertainty assessment framework for tritium-inferred transit time estimations under baseflow conditions. *Hydrological Processes*, 30(25), 4741–4760. <https://doi.org/10.1002/hyp.10991>
- Grabczak, J., Rózański, K., Maloszewski, P., & Zuber, A. (1984). Estimation of the tritium input function with the aid of stable isotopes. *Catena*, 11(2-3), 105–114. [https://doi.org/10.1016/0341-8162\(84\)90001-8](https://doi.org/10.1016/0341-8162(84)90001-8)
- Hargreaves, G. H., & Samani, Z. A. (1982). Estimating potential evapotranspiration. *Journal of the irrigation and Drainage Division*, 108(3), 225–230.
- Hrachowitz, M., Soulsby, C., Tetzlaff, D., Dawson, J. J. C., Dunn, S. M., Malcolm, I. A. 2009. Using long-term data sets to understand transit times in contrasting headwater catchments. *Journal of Hydrology* 367: 237–248, <https://doi.org/10.1016/j.jhydrol.2009.01.001>
- Jacobs, S., Rufino, M., Butterbach Bahl, K., Timbe Castro, E. P., Weeser, B., & Breuer, L. (2018). Assessment of hydrological pathways in East African montane catchments under different land use. *Hydrology and Earth System Sciences*, 22, 4981–5000. <https://doi.org/10.5194/hess-22-4981-2018>
- Jasechko, S., Kirchner, J. W., Welker, J. M., & McDonnell, J. J. (2016). Substantial proportion of global streamflow less than three months old. *Nature Geoscience*, 9(2), 126. <https://doi.org/10.1038/NGEO2636>
- Jasechko, S., S. J. Birks, T. Gleeson, Y. Wada, P. J. Fawcett, Z. D. Sharp, J. J. McDonnell & J. M. Welker (2014), The pronounced seasonality of global groundwater recharge, *Water Resources Research*, 50, 8845–8867, <https://doi.org/10.1002/2014WR015809>.
- Jasechko, S., Wassenaar, L. I., & Mayer, B. (2017). Isotopic evidence for widespread cold-season-biased groundwater recharge and young streamflow across central Canada. *Hydrological processes*, 31(12), 2196–2209. <https://doi.org/10.1002/hyp.11175>
- 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, 279–297. <https://doi.org/10.5194/hess-20-279-2016>
- 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, 299–328. <https://doi.org/10.5194/hess-20-299-2016>.
- Kirchner, J. W. (2019). Quantifying new water fractions and transit time distributions using ensemble hydrograph separation: theory and benchmark tests. *Hydrology & Earth System Sciences*, 23(1). <https://doi.org/10.5194/hess-23-303-2019>
- Kirchner, J. W. & Allen, S. T. (2020) Seasonal partitioning of precipitation between streamflow and evapotranspiration, inferred from end-member splitting analysis, *Hydrology & Earth System Sciences*, 24, 17–19. <https://doi.org/10.5194/hess-24-17-2020>
- Kirchner, J. W., Feng, X., Neal, C., & Robson, A. J. (2004). The fine structure of water-quality dynamics: the (high-frequency) wave of the future. *Hydrological Processes*, 18(7), 1353–1359. <https://doi.org/10.1002/hyp.5537>

- Latron, J. & Gallart, F. (2007). Seasonal dynamics of runoff-contributing areas in a small Mediterranean research catchment (Vallcebre, Eastern Pyrenees). *Journal of Hydrology* 335 (1), 194-206. <https://doi.org/10.1016/j.jhydrol.2006.11.012>.
- Latron, J. & Gallart, F. (2008). Runoff generation processes in a small Mediterranean research catchment (Vallcebre, Eastern Pyrenees). *Journal of Hydrology*, 358(3-4), 206-220. <https://doi.org/10.1016/j.jhydrol.2008.06.014>.
- Latron, J., Llorens, P. & Gallart, F. (2009). The hydrology of Mediterranean mountain areas. *Geography Compass* 3 (6), 2045-2064. <https://doi.org/10.1111/j.1749-8198.2009.00287.x>.
- Latron, J., Roig-Planasdemunt, M., Llorens, P. & Gallart, F. (2015). Combining stable isotopes and hydrometric data to investigate the stormflow response of a Mediterranean mountain catchment (Vallcebre Research Catchments, Spain), *Geophysical Research Abstracts* 17.
- Latron, J., Soler, M., Llorens, P. & Gallart, F. (2008). Spatial and temporal variability of the hydrological response in a small Mediterranean research catchment (Vallcebre, Eastern Pyrenees). *Hydrological Processes* 22, 775-787. <https://doi.org/10.1002/hyp.6648>.
- Llorens, P., Gallart, F., Cayuela, C., Planasdemunt, M. R., Casellas, E., Molina, A. J., Moreno-de-las-Heras, M., Bertran, G., Sánchez-Costa, E. & Latron, J. (2018). What have we learnt about Mediterranean catchment hydrology? 30 years observing hydrological processes in the Vallcebre research catchments. *Cuadernos de Investigación Geográfica / Geographical Research Letters*, (44), 475-502. <http://doi.org/10.18172/cig.3432>
- Llorens, P., Latron, J., & Gallart, F. (1992). Analysis of the role of agricultural abandoned terraces on the hydrology and sediment dynamics in a small mountainous basin (High Llobregat, Eastern Pyrenees). *Pirineos*, 139, 27-46. <https://doi.org/10.3989/pirineos.1992.v139.180>
- Lutz, S. R., Krieg, R., Müller, C., Zink, M., Knöller, K., Samaniego, L., & Merz, R. (2018). Spatial patterns of water age: Using young water fractions to improve the characterization of transit times in contrasting catchments. *Water Resources Research*, 54, 4767–4784. <https://doi.org/10.1029/2017WR022216>.
- Maloszewski, P., Rauert, W., Stichler, W., & Herrmann, A. (1983). Application of flow models in alpine catchment area using tritium and deuterium data, *Journal of Hydrology*, 66, 319-330. [https://doi.org/10.1016/0022-1694\(83\)90193-2](https://doi.org/10.1016/0022-1694(83)90193-2)
- Martín-Gómez, P., Barbeta, A., Voltas, J., Peñuelas, J., Dennis, K., Palacio, S., Dawson, T.E. & Ferrio, J. P. (2015). Isotope-ratio infrared spectroscopy: a reliable tool for the investigation of plant-water sources?. *New Phytologist*, 207(3), 914-927. <https://doi.org/10.1111/nph.13376>
- McDonnell, J. J., & K. Beven (2014), Debates—The future of hydrological sciences: A common) path forward? A call to action aimed at understanding velocities, celerities, and residence time distributions of the headwater hydrograph, *Water Resources Research*, 50, 5342–5350, <https://doi.org/10.1002/2013WR015141>.
- McGuire KJ, McDonnell JJ. (2006). A review and evaluation of catchment transit time modelling. *Journal of Hydrology* 330: 543–563. <https://doi.org/10.1016/j.jhydrol.2006.04.020>
- Neal, C., Reynolds, B., Rowland, P., Norris, D., Kirchner, J. W., Neal, M., Sleep, D., Lawlor, A., Woods, C., Thacker S., Guyatt, H., Vincent, C., Hockenhull, K., Wickham, H. & Guyatt, H. (2012). High-frequency water quality time series in precipitation and streamflow: From fragmentary signals to scientific challenge. *Science of the Total Environment*, 434, 3-12. <https://doi.org/10.1016/j.scitotenv.2011.10.072>

- Poyatos, R., Latron, J. & Llorens, P. (2003). Land use and land cover change after agricultural abandonment - The case of a Mediterranean mountain area (Catalan Pre-Pyrenees). *Mountain Research and Development* 23 (4), 362-368. [https://doi.org/10.1659/0276-4741\(2003\)023\[0362:LUALCC\]2.0.CO;2](https://doi.org/10.1659/0276-4741(2003)023[0362:LUALCC]2.0.CO;2).
- Remondi, F., Botter, M., Burlando, P., & Fatichi, S. (2019). Variability of transit time distributions with climate and topography: A modelling approach. *Journal of hydrology*, 569, 37-50. <https://doi.org/10.1016/j.jhydrol.2018.11.011>
- Rubio, C.M., Llorens, P. & Gallart, F. (2008). Uncertainty and efficiency of pedotransfer functions for estimating water retention characteristics of soils. *European Journal of Soil Science* 59 (2), 339-347. <https://doi.org/10.1111/j.1365-2389.2007.01002.x>.
- Solé, A., Gallart, F., Pardini, G. & Aringhieri, R. (1992). How mudrock and soil physical properties influence badland formation at Vallcebre (Pre-Pyrenees, NE Spain). *Catena* 19 (3-4), 287-300. [https://doi.org/10.1016/0341-8162\(92\)90003-T](https://doi.org/10.1016/0341-8162(92)90003-T).
- Song, C., Wang, G., Liu, G., Mao, T., Sun, X., & Chen, X. (2017). Stable isotope variations of precipitation and streamflow reveal the young water fraction of a permafrost watershed. *Hydrological Processes*, 31(4), 935-947. <https://doi.org/10.1002/hyp.11077>.
- Soulsby, C., Piegat, K., Seibert, J., & Tetzlaff, D. (2011). Catchment-scale estimates of flow path partitioning and water storage based on transit time and runoff modelling. *Hydrological Processes*, 25(25), 3960-3976. <https://doi.org/10.1002/hyp.8324>
- Soulsby, C., C. Birkel, J. Geris, J. Dick, C. Tunaley, & D. Tetzlaff (2015), Stream water age distributions controlled by storage dynamics and nonlinear hydrologic connectivity: Modeling with high-resolution isotope data, *Water Resources Research*, 51, 7759–7776, <https://doi.org/10.1002/2015WR017888>.
- Soulsby, C., C. Birkel, & D. Tetzlaff (2016), Characterizing the age distribution of catchment evaporative losses, *Hydrological Processes*, 30(8),1308–1312, <https://doi.org/10.1002/hyp.10751>.
- Sprenger, M., Llorens, P., Cayuela, C., Gallart, F., & Latron, J. (2019a). Mechanisms of consistently disjunct soil water pools over (pore) space and time. *Hydrology and Earth System Sciences*, 23(6), 2751-2762. <https://doi.org/10.5194/hess-23-2751-2019>.
- Sprenger, M., Stumpp, C., Weiler, M., Aeschbach, W., Allen, S. T., Benettin, P. Dubbert, M., Hartmann, A., Hrachowitz, M., Kirchner, J.W., McDonnell, J.J., Orlowski, N., Penna, D., Pfahl, S., Rinderer, M., Rodriguez, N., Schmidt, M. & Werner, C.h, (2019b). The demographics of water: A review of water ages in the critical zone. *Reviews of Geophysics*, 57, 3: 800-834. <https://doi.org/10.1029/2018RG000633>
- Steenhuis, T. S., & Van der Molen, W. H. (1986). The Thornthwaite-Mather procedure as a simple engineering method to predict recharge. *Journal of Hydrology*, 84(3-4), 221-229. [https://doi.org/10.1016/0022-1694\(86\)90124-1](https://doi.org/10.1016/0022-1694(86)90124-1)
- Stewart, M.K., Morgenstern, U. & McDonnell, J.J. (2010). Truncation of stream residence time: how the use of stable isotopes has skewed our concept of streamwater age and origin. *Hydrological Processes* 24: 1646–1659. <https://doi.org/10.1002/hyp.7576>
- Stewart, M.K., Morgenstern, U., McDonnell, J.J. & Pfister, L. (2012). The ‘hidden streamflow’ challenge in catchment hydrology: a call to action for stream water transit time analysis. *Hydrological Processes* 26: 2061–2066. <https://doi.org/10.1002/hyp.9262>
- Stockinger, M. P., Bogen, H. R., Lücke, A., Diekkrüger, B., Cornelissen, T., & Vereecken, H. (2016). Tracer sampling frequency influences estimates of young water fraction and

streamwater transit time distribution. *Journal of hydrology*, 541, 952-964. <http://dx.doi.org/10.1016/j.jhydrol.2016.08.007>

Stockinger, M. P., Bogen, H. R., Lücke, A., Stumpp, C., & Vereecken, H. (2019). Time variability and uncertainty in the fraction of young water in a small headwater catchment. *Hydrology and Earth System Sciences*, 23(10), 4333-4347. <https://doi.org/10.5194/hess-23-4333-2019>.

Tetzlaff, D., Malcolm, I. A., & Soulsby, C. (2007). Influence of forestry, environmental change and climatic variability on the hydrology, hydrochemistry and residence times of upland catchments. *Journal of Hydrology*, 346(3-4), 93-111. Wilusz, D. C., Harman, C. J., & Ball, W. P. (2017). Sensitivity of catchment transit times to rainfall variability under present and future climates. *Water Resources Research*, 53, 10,231–10,256. <https://doi.org/10.1002/2017WR020894>

Zhang, Q., Knowles, J. F., Barnes, R. T., Cowie, R. M., Rock, N., & Williams, M. W. (2018). Surface and subsurface water contributions to streamflow from a mesoscale watershed in complex mountain terrain. *Hydrological processes*, 32(7), 954-967. <https://doi.org/10.1002/hyp.11469>

Supporting Information

Additional Supporting Information on the ‘effective precipitation’ may be found in the corresponding file available with the online version of this article.

Tables

Table 1: Main statistics of the ^{18}O analyses during the sampling periods. Precipitation and simulated recharge isotopic signatures were volume-weighted. Soil water (Sw) was sampled with low suction lysimeters. Shallow (sh) and deep (dp) groundwater (Gw) at VP05 refers to samples taken when water table levels were respectively shallower or deeper than 2.25 m.

$\delta^{18}\text{O}$ (‰)	Precipitation	Simulated recharge	Sw VL01	Sw VL02	Gw VP01
Maximum	0.86	-0.10	-4.63	-4.78	-6.09
Minimum	-19.12	-17.86	-8.58	-8.01	-8.12
Mean	-7.15	-7.90	-6.66	-6.68	-6.81
Std. Dev.	3.30	3.12	1.09	0.78	0.58

$\delta^{18}\text{O}$ (‰)	Gw VP05	Gw VP05 sh	Gw VP05 dp	Time-weighted Stream water	Flow-weighted Stream water
Maximum	-6.10	-6.10	-6.45	-5.50	-5.50
Minimum	-7.99	-7.99	-7.56	-13.50	-13.50
Mean	-7.04	-7.13	-6.93	-7.21	-7.39
Std. Dev.	0.42	0.49	0.29	0.39	1.03

Table 2: Mean ^{18}O signatures and differences in diverse hydrological compartments with respect to precipitation and simulated recharge waters. Differences in **bold** are significant at the 1% level and underlined differences are significant at the 5% level (Student's t test, two tails). VW means volume-weighted, TW means time-weighted and FW means flow-weighted statistics. Soil water (Sw) was sampled with low suction lysimeters. Sh and dp groundwater (Gw) at VP05 refer to samples taken when water table levels were, respectively, shallower or deeper than 2.25 m.

$\delta^{18}\text{O}$ (‰)	Precipitation VW	Recharge VW	Sw VL01	Sw VL02	Gw VP01	Gw VP05	Gw VP05 sh	Gw VP05 dp	Stream TW	Stream FW
Mean	-7.24	-7.90	-6.66	-6.68	-6.81	-7.01	-7.08	-6.93	-7.21	-7.39
Std. error	0.292	0.407	0.137	0.128	0.097	0.055	0.089	0.052	0.027	0.080
- Precipitation		-0.66	0.58	0.56	<u>0.43</u>	0.23	0.16	<u>0.31</u>	0.03	-0.15
- Recharge			1.24	1.22	1.09	<u>0.89</u>	<u>0.82</u>	<u>0.97</u>	<u>0.69</u>	0.51

Table 3: Characteristics of the sinusoid functions and young water fractions obtained by the application of Eq. (1) to all the studied water compartments. Level-weighted groundwater (Gw) VP05 corresponds to the results for groundwater at VP05 when the isotopic signature was weighted with the exponent of the water table level. Shallow groundwater means depth to the water table was between 0 and 2.25 m; and deep groundwater, that it was deeper than 2.25 m. A is the amplitude, k is the zero value and ϕ is the phase shift of the fitted sinusoid functions. F_{yw} is the young water fraction calculated with Eq. (2), using precipitation

A as input amplitude (A_p). The abbreviation n. s. means that the value was not significantly different from 0. F_{yw} and F_{yw}^* refer to time-weighted and flow-weighted young water fractions, respectively, when estimated for stream waters. (1) denotes dimensionless variables.

Compartment	A (‰)	k (‰)	φ (days)	F_{yw} / F_{yw}^* (1)
Precipitation	3.01 ± 0.22	-7.99 ± 0.15	115.7 ± 3.5	-
Simulated recharge	2.35 ± 0.38	-7.81 ± 0.19	114.4 ± 3.8	-
Sw VL01	1.03 ± 0.18	-6.61 ± 0.11	148.2 ± 8.2	0.344 ± 0.064
Sw VL02	0.62 ± 0.18	-6.62 ± 0.12	137.6 ± 14.4	0.207 ± 0.062
Gw VP01	n. s.	-6.89 ± 0.11	-	n. s.
Gw VP05	0.24 ± 0.08	-7.02 ± 0.05	137.6 ± 14.4	0.078 ± 0.026
Level-weighted Gw VP05	0.35 ± 0.10	-7.07 ± 0.06	144.6 ± 12.7	0.115 ± 0.033
Shallow Gw VP05	0.63 ± 0.15	-6.98 ± 0.08	150.4 ± 8.5	0.209 ± 0.051
Deep Gw VP05	n. s.	-6.92 ± 0.05	-	n. s.
Stream, time-weighted	0.19 ± 0.02	-7.21 ± 0.01	181.6 ± 5.8	0.062 ± 0.008
Stream, flow-weighted	0.68 ± 0.07	-7.43 ± 0.04	132.9 ± 3.6	0.226 ± 0.028

Table 4: Summary of the metrics obtained with the different sampling strategies and weighting methods. FW means flow-weighting, TW means time-weighting. Grey figures are not significantly different from 0. F_{yw}^{**} , F_{yw}^* and F_{yw} refer, respectively, to virtual sampling FW, dynamic and weekly sampling FW and dynamic and weekly sampling TW estimates of young water fractions. (1) denotes dimensionless variables.

Sampling and weighting methods	$F_{yw}^{**} / F_{yw}^* / F_{yw}$ (1)	F_0 (1)	S_d (d mm ⁻¹)
Virtual sampling FW	0.304 ± 0.030	-	-
Dynamic sampling FW	0.226 ± 0.028	0.024 ± 0.028	0.056 ± 0.010
Weekly sampling FW	0.103 ± 0.033	0.018 ± 0.046	0.018 ± 0.008
Dynamic sampling TW	0.062 ± 0.008	0.038 ± 0.007	0.035 ± 0.008
Weekly sampling TW	0.044 ± 0.014	-0.002 ± 0.015	0.025 ± 0.012

Figure legends

Figure 1: Map of the Can Vila catchment, showing the main land cover types and the location of the instruments and sampling sites used for this study.

Figure 2: Isotopic ratios of all the precipitation samples compressed into a one-year period. Non-effective points represent the samples that were tentatively discarded as evapotranspired after the recharge model. Lines represent the seasonal variations according to the best fits of Eq. (1) for the gross precipitation and the simulated (effective) recharge weightings.

Figure 3: Isotopic ratios of mobile soil and ground water samples compressed into a one-year period. Lines represent the seasonal variations according to the best fits of Eq. (1), the dashed line showing that the amplitude A was not significantly different from 0 for VP01.

Figure 4: Variation of the isotopic ratios of ground water with water table level at VP05. The grey line separates the shallow and deep water levels analysed in Tables 1, 2 and 3.

Figure 5: Stream discharge (5-minute step) and isotopic ratios of stream waters during the recorded period.

Figure 6: $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ plot of the precipitation, soil and stream waters, along with the Local Meteoric Water Line.

Figure 7: Variation in time-weighted young water fraction at the Can Vila catchment with increasing quantiles of the flow duration curve. The curve represents Eq. (5), using parameters obtained by fitting Eq. (6) to all the stream water $\delta^{18}\text{O}$ isotope values. Maximum sampled discharge was 226 mm d^{-1} . Vertical bars represent standard errors. (1) denotes a dimensionless variable. Reproduced from Gallart *et al.* (2020).

Figure 8: Time thresholds τ_{yw} for the definition of the young water fractions of soil waters (VL), ground waters (VP) and stream waters smaller than 1 shown in Figure 7, after Eqs. (3) and (4). Bars represent 90% confidence intervals. (1) denotes a dimensionless variable.

Figure 9: Flow-weighted young water fractions (F_{yw}^*) and discharge sensitivities of young water fraction (S_d) for 6 one-year windows and the full record available at Can Vila. Q represents discharge. Bars represent standard errors. (1) denotes a dimensionless variable.

Figure 10: Comparison between relative cumulative time, flow and F_{yw}^* simulated by applying Eq. (5) to the 5-minute step flow record, as well as the relative cumulative flows for the dynamic and weekly sampling records. The 1:1 line is shown as a reference for a uniform distribution.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10