What drives F_{yw} variations Towards a conceptualization of the hydrological processes behind changes of young water fraction with elevation in Alpine: a focus on mountainous alpine catchments?

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Abstract. The young water fraction $(F_{yw}F_{yw}^*)$, defined as the fraction of catchment outflow with transit times of less than about 2-3 months, is increasingly used in hydrological studies, replacing that exploit the widely used Mean Transit Time (*MTT*), which is subject to aggregation errorpotential of isotope tracers. The use of this new metric in catchment intercomparison studies is helpful to understand and conceptualize the relevant processes controlling eatehment's

- 20 hydrological function.catchment functioning. Past work hasworks have shown the remarkable and counterintuitivesurprising evidence that steep (and generally high elevation)mountainous catchments worldwide reveal small F_{ym}yield low F^{*}_{ym}. These low values. However, the topographic slope only have been partially explains the observed F_{ym} variance, and theexplained by isolated hydrological processes, including deep vertical infiltration and long groundwater flow paths. However, a harmonious framework illustrating the relevant mechanisms hidden behind this lowering with slope remain basically unelearleading to a low F^{*}_{ym} in mountainous catchments is missing.
- The main aim of this paper is to investigate-give an overview of what drives $F_{\mu\nu}F^*_{\nu\nu}$ variations with according to elevation in Alpine catchments, thus clarifying why $F_{\mu\nu}$ is lowit generally decreases at high altitudes. In elevation. For this regardpurpose, we use assembled a dataset composed data set of 27 study catchments, located both inacross Switzerland and in-Italy, that we categorize as rainfall dominated, hybrid or for which $F^*_{\mu\nu}$ values are available or have been calculated. We
- 30 assume that this decrease can be explained by the groundwater storage potential, quantified by the areal extent of Quaternary deposits over a catchment (F_{ad}), and the low-flow duration (LFD) throughout the period of isotope sampling (PoS). In snowdominated according to a proposed formal classification scheme that considers both a common-used monthly streamflow ratio and the snow cover regime. We analyze three not previously investigated variables that could potentially explain the F_{pw} -elevation gradients: the systems, LFD is strictly related to the snowpack persistence, quantified from Sentinel-2 L2A

35 satellite images through the average fractional snow cover area (*F_{SCA}*), the fraction of quaternary deposits (*F_{qd}*), and the fraction of). The drivers under study are directly or indirectly related to the catchment storage contribution to the stream, that we quantify applying a cutting-edge baseflow separation method to the discharge time series of the study sites and estimating the average baseflow fraction (*F_{bf}*). We also consider a fourth variable, namely the Winter Flow Index (*WFI*), for comparing our results about the groundwater contribution to streamflow with those of previous scientific publications-) over 40 the PoS.

Our results suggest that unconsolidated sedimentsQuaternary deposits could potentially play a role in modulating $F_{yw}F^*_{yyv}$ elevation gradients via their capacity to store groundwater, but <u>a future confirmation with</u> further, more detailed geological information, such as the portion of fractured bedrocks, would be desirable for a complete picture of the role of geology. Based on our analysis concerning the F_{SC47-} is necessary. LFD measures the proportion of PoS in which the stream is

- 45 sustained and dominated by stored (old) water coming from the catchment storage. Accordingly, our results reveal that the increase of LFD at high elevations, to a large extent driven by the persistence of winter snowpacks and the simultaneous lack of a liquid water input to the catchments, results in lower F^*_{yw} . In our data set F_{bf} reveals a strong complementarity with F^*_{yw} , suggesting that the latter could be estimated as $F^*_{yw} \simeq 1 F_{bf}$ for catchments in which stable water isotopes measurements are not available.
- 50 As a conclusion, we develop a perceptual model that explains how the increasing duration of the snowpack promotes a progressive emptying of the groundwater storage during winter, thereby increasing the streamwater age, while ephemeral snowpack generally favors rapid flow paths that increase F_{ywr} . Finally, our work highlights that F_{bf} , considered as a proxyintegrates all the results of our analysis to describe a framework for groundwater flow, is roughly the one's complement of F_{ywr} . In harmony with the model, we find high F_{bf} during all low-flow periods, which underlines that
- 55 streamflow is mainly sustained by groundwater in such flow conditions. For catchments where the winter low-flow period is long compared to the summer high-flow period, this results in low F_{yw} how hydrological processes control F^*_{yw} according to elevation, laying the foundations for an improvement of the theory-driven models.

In conclusion, our data set suggests that F_{bf} is the best explanatory variable of F_{yw} elevation gradients in Alpine catchments, implying the key-role of major groundwater storages that, with the increasing snowpack duration, are actively involved in
 streamflow generation processes.

1 Introduction

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AlpineMountainous alpine catchments are often assumed to generate a high shareshares of rapid surface or subsurface runoff due to the presence of exposed bedrock and steep landscapes, consequently. Consequently, the role of groundwater storage in high-elevation catchments has been often neglected (Hayashi, 2020). However, early work in the Swiss Alps showed that high celerity is caused by the release of groundwater to the stream, so that the streamflow is older than the annual snowmeltOn the contrary, multiple worldwide studies quantified a considerable groundwater input to streamflow in high

mountain catchments using tracer or water balance-(Martinee, 1975). This corresponds to results obtained through stableisotope based hydrograph separation performed in 101 studies worldwide that revealed that more than half of streamflow is composed of groundwater even during no-rain and no-snowmelt periods (Jasechko, 2019). To date, it is well known that the

70 age of water stored in catchments is well beyond the annual timescale and that it plays a key role in streamflow generation processes (McDonnell, 2017; Jasechko, 2019). In this regard, the hydrological community expressed the need for better understanding of transit time distributions in the terrestrial water cycle (Blöschl et al., 2019).

The study of water age is crucial for predicting the timing of nutrient cycles and pollutant transport since water age and solute dynamics can be coupled (Jasechko et al., 2016; Benettin et al., 2017).-However, water age quantification is not straight forward. Kirchner (2016a, b) proposed a new metric to quantify water age at the catchment scale: the young water

- 75 straight forward. Kirchner (2016a, b) proposed a new metric to quantify water age at the catchment seale: the young water fraction (*F_{yw}*), defined as the fraction of catchment outflow with transit times of less than roughly 0.2 years (Kirchner, 2016a). It can be conveniently inferred from the dampening effect that a catchment has on the seasonal cycle of stable water isotopes in precipitation, i.e. by estimating the amplitude ratio of the seasonal cycle of stable water isotopes in streamflow to that of precipitation (Kirchner, 2016a). The *F_{yw}*-concept has rapidly supplanted the similar metric, Mean Transit Time
- 80 (MTT), because it has the advantage of being free from the aggregation errors inherent to MTT. The F_{yw} is also an informative proxy of a catchment's hydrological function, in terms of water partitioning and release (Stockinger et al., 2019). Therefore, this new metric is useful for catchment intercomparison studies to analyze the main hydro-climatic and landscape characteristics that influence the transit times of water (von Freyberg et al., 2018). Indeed, some studies have already tried to find a relationship between young water fractions and catchment characteristics. von Freyberg et al. (2018)
- 85 found that young water fractions of 22 Swiss catchments are positively correlated (with statistical significance) with selected hydro-elimatic indices and the fraction of saturated area, suggesting that F_{yw} depends on catchment wetness which promotes rapid flow paths.

Interestingly, the analysis by von Freyberg et al. (2018) revealed that the young water fraction is positively correlated with mean catchment elevation, but only when the 5 high elevation, snow dominated catchments are omitted from the analysis.
Indeed, Ceperley et al. (2020), who compared the F_{yw} from three additional high elevation catchments to the original dataset of von Freyberg et al. (2018), observe a drop of F_{yw} above 1500 m a.s.l., to which we refer hereafter as F_{yw}-reset. In line with these findings, a recent study estimated F_{yw} for 24 catchments in Germany and observed the smallest values in mountainous landscapes (Lutz et al., 2018).

This F_{yw}-reset is partially consistent with the counterintuitive outcomes of Jasechko et al. (2016) whose work reveals that young streamflow is less prevalent in steep (and generally high) landscapes. They explain this by a consistent deep vertical infiltration component for such steep high elevation catchments (Jasechko et al., 2016). However, even if the topographic gradient is correlated with the young water fraction in the 254 watersheds data set of Jasechko et al. (2016), the relationship is relatively scattered, leaving a large portion of variance unexplained and suggesting that other variables can play a key role in reducing F_{yw} according to slope steepness or with elevation (Jasechko et al., 2016).



- 100 Comparing different F_{yw} estimation methods in presence of snow-in the Swiss and Italian Alps, Ceperley et al. (2020) observed that high Alpine catchments reveal low F_{yw}. Therefore, the snow storage could have a role in decreasing the young water fraction. The elevation of 1500 m a.s.l., above which we have the F_{yw} reset, has been previously identified as corresponding to the transition between intermittent and seasonal snow cover (Santos et al., 2018). However, it is unclear if the snow cover dynamics can lead to a more efficient groundwater recharge, consequently reducing or increasing the young streamflow reaching the stream (Ceperley et al., 2020).
- Tracer or water balance methods are powerful tools to quantify groundwater contribution to rivers and multiple worldwide studies have estimated the considerable groundwater input to streamflow in high mountain catchments using such methods (Somers and McKenzie, 2020). Several eatchmentsstudies located in the Rocky Mountains and Andes mountain ranges show that remarkable fractions, on average, about 47% of groundwater annually sustainsustains the streamflow (Saberi et al.,
- 110 2019; Somers et al., 2019; Carroll et al., 2018; Harrington et al., 2018; Cowie et al., 2017; Baraer et al., 2015; Gordon et al., 2015; Frisbee et al., 2011; Liu et al., 2004; Clow et al., 2003; Baraer et al., 2009)(Saberi et al., 2019; Somers et al., 2019; Carroll et al., 2018; Harrington et al., 2018; Cowie et al., 2017; Baraer et al., 2009)(Saberi et al., 2015; Frisbee et al., 2011; Liu et al., 2018; Cowie et al., 2017; Baraer et al., 2015; Gordon et al., 2015; Frisbee et al., 2011; Liu et al., 2004; Clow et al., 2003; Baraer et al., 2009). This result isSimilar results are also found in the Himalayas (49%) and the Alps mountain ranges(48%) (Chen et al., 2018; Engel et al., 2016; Käser and Hunkeler, 2016; Williams et al., 2016;
- Wilson et al., 2016; Andermann et al., 2012). To date, it is well known that the age of water stored in catchments is well beyond the annual timescale and that it plays a key role in streamflow generation processes (McDonnell, 2017; Jasechko, 2019). The study of water age is crucial for predicting the timing of nutrient cycles and pollutant transport since water age and solute dynamics are closely coupled (Li et al., 2021). However, water age quantification is not straight forward. There is however still a lack of understanding regarding the mechanisms that lead to a dynamic storage contribution to streamflow (Kirchner, 2003) and, consequently, how this contribution impacts the young water fraction.
- Kirchner (2016a, b) proposed a new metric to quantify the share of catchment outflow with transit times lower than roughly 0.2 years or 2-3 months: the young water fraction. This metric can be conveniently inferred from the dampening effect that a catchment has on the seasonal cycle of stable water isotopes in precipitation, i.e. by estimating the ratio of the amplitudes of the seasonal cycles of stable water isotopes in streamflow and in precipitation (Kirchner, 2016a). In this method, the
- 125 seasonal cycle of stream water isotope measurements is modelled using a sine wave that can be flow-weighted or not, using as weights the discharge measured at the moment of sampling (von Freyberg et al., 2018). Isotopes measured in precipitation can be modelled with a sine function weighted according to the volume of precipitation, to reduce the influence of low-precipitation periods and to account for temporally aggregated rainfall samples (von Freyberg et al., 2018). Flowweighted fits to the seasonal tracer cycles predict the flow-weighted average young water fraction (*F**_{yw}) in streamflow,
- 130 while unweighted fits to the seasonal tracer cycles predict the unweighted one (F_{yyy}) (Kirchner, 2016b). Gallart et al. (2020a) recently highlighted the advantages of the flow-weighted analysis to compensate for subsampled high-flow periods, thus

reducing the underestimation of the young water fraction. Hereafter, we will use the symbol '*' for referring to a flowweighted variable, in order to be consistent with previous studies (von Freyberg et al., 2018; Gallart et al., 2020a).

- F*_{yw} is increasingly used in hydrological studies because it has the advantage of being free from the aggregation errors
 inherent to Mean Transit Time (MTT) estimates obtained through the classical convolution approach (Kirchner, 2016a).
 Even more so, F*_{yw} is an informative descriptor of catchment hydrological functions, of nutrients cycles and of pollutant transport (Stockinger et al., 2019; Benettin et al., 2017; Jasechko et al., 2016). Therefore, this new metric is useful for catchment intercomparison studies to find what are the main hydro-climatic and landscape characteristics that drive the transit times of water lower than 2-3 months. Indeed, past works have tried to study the relationship between F*_{yw} and
- 140 catchment characteristics. von Freyberg et al. (2018) found that young water fractions of 22 Swiss catchments are positively correlated (with statistical significance) with selected hydro-climatic indices and with the fraction of saturated area, suggesting that F^*_{yw} depends on catchment wetness, which promotes rapid flow paths. Interestingly, in their data set, a statistically significant positive correlation with elevation was obtained after removing from their analysis the five snow-dominated catchments, which revealed the smallest F^*_{yw} values (von Freyberg et al., 2018). Likewise, Lutz et al. (2018)
- 145 estimated F*_{yw} for 24 catchments in Germany and found the smallest values for higher-elevation sites. These results are partially consistent with those of Jasechko et al. (2016): based on the analysis of 254 watersheds worldwide, their work revealed a reduction of F*_{yw} in mountainous, steeper terrains. This could be related to deep vertical infiltration caused by fractures generated by high rock stress in complex terrain morphologies or by freely draining soils (i.e., cambisols and luvisols), both associated to high-elevation environments (Lutz et al., 2018; Jasechko et al., 2016; Gleeson et al., 2014). In
- 150 addition, the higher the topographic roughness is, the longer are the flow paths, with a consequent rise of transit times (Gleeson and Manning, 2008; Frisbee et al., 2011; Jasechko et al., 2016). Despite of these studies, there is still a lack of a harmonious framework of how the relevant drivers and hydrological processes in mountainous catchments lead to a small percentage of young water at high elevation, leaving this result basically unclear.

An early work in the Swiss Alps shows that high celerity is caused by massive meltwater infiltration that pushes out
 groundwater reserves: streamflow following snowmelt is older than meltwater infiltrated in the current year (Martinec, 1975). The resulting effect on water partitioning between the surface and the subsurface should be analyzed considering the temporal concentration of water input on the snowmelt period, but this remains largely unexplored to date (Rey et al., 2021). Despite of this lack of studies on water partitioning during snowmelt, several studies have demonstrated the pivotal role of snowmelt in recharging groundwater during summer in high-elevation environments (Hayashi, 2020; Cochand et al., 2019; Du et al., 2019; Flerchinger et al., 1992).

From a water storage perspective, and thus from a water age perspective, snowpack storage and groundwater storage can be considered as a single entity: they both constitute catchment storage. Therefore, the analytical estimation of F^*_{yw} must reflect this "conceptual" decision of considering the snowpack storage as part of the catchment storage or not. This point has been previously addressed by von Freyberg et al. (2018): if total precipitation is considered as catchment input (what can be called

- 165 the direct input case), the snowpack is implicitly considered as part of the catchment storage and F^*_{yw} results from the combination of snowpack and subsurface storage. In this direct input case, F^*_{yw} is computed from the amplitudes of the seasonal cycles of stable isotopes of water in precipitation (A_P) and in streamflow (A^*_s) . If total *liquid* water input (composed of rainfall and snowmelt, sometimes called equivalent precipitation) is considered as catchment input, F^*_{yw} is computed based on the amplitudes of the cycles in equivalent precipitation (A_{Peq}) and in streamflow (A^*_s) . This F^*_{yw} value then results
- 170 from subsurface storage alone, since snowpack storage is excluded from the catchment storage (von Freyberg et al., 2018). If *F*_{yw}* is estimated using a direct input setting (i.e., total precipitation directly), *F*_{yw}* is expected to be smaller since the catchment storage is larger (von Freyberg et al., 2018). Also, Ceperley et al. (2020) investigated the role of water input from snow in *F*_{yw}* estimation, concluding that the low values in high alpine snow-dominated catchments result from a combination of snow cover effects and the storage in the subsurface. In the present work, the main aim is not to focus on
- 175 how the snowpack affects F*_{yw} estimation in a single catchment, as this was treated in previous works (von Freyberg et al., 2018; Ceperley et al., 2020), but to investigate the hydrological processes (also related to the snowpack storage) that lead to changes in F*_{yw} between catchments located at different elevations, focusing on high-elevation alpine catchments. Some authors have revealed the possibility of quaternary deposits (e.g., talus, moraine, alluvium) to store groundwater in
- high-elevation alpine catchments (Arnoux et al., 2021; Hayashi, 2020; Christensen et al., 2020). The stored water in these
 deposits can in fact sustain streamflow during the low-flow period (Hayashi, 2020; Arnoux et al., 2021), Moreover, recent streamflow data based and model based studies in the Swiss Alps point towards important mobile groundwater storage in high elevation catchments, which could be related to quaternary deposits: e.g., moraines, alluvium, and talus (Staudinger et al., 2017; Cochand et al., 2019; Arnoux et al., 2021). Therefore, it is necessary to understand the capability of unconsolidated sediments of storing high-mountain groundwater and how this geology influences the amount of young water reaching the stream.

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Accordingly, we study here a new set of hydrological variables to gain new insights into the F_{yw} along elevation gradients: the fractional snow cover area (F_{SC4}), the fraction of quaternary deposits (F_{qd}) and the fraction of baseflow (F_{bf}), defined in detail in Sections 3.4 and 3.5. We also consider a fourth index, namely the Winter Flow Index (*WFI*), for testing consistency of our results with those of a past study (Arnoux et al., 2021) that used this index to quantify the groundwater contribution

190 to streamflow.

In the following, we first classify the study catchments, described in Section 2, into three hydro-climatic regimes proposing a new criterion of classification (Section 3.3). Then, we study the correlation of the selected hydrological variables with the young water fraction (Sections 4.3.1, 4.3.2, 4.3.3) and we finally bring these results back to the ongoing scientific discussion of F_{two} (Section 5).

195 as supported by the strong positive correlation found by Arnoux et al. (2021) between the fraction of quaternary deposits and the Winter Flow Index (a low-flow indicator reflecting the groundwater contribution to the stream) for 13 alpine catchments . During winter, the period without liquid water input can last 6 months or more in high elevation catchments. Such sustained

flow during long periods points towards important amounts of stored water (or old water) that are well connected to the stream network and thereby remains accessible throughout the low flow period. (Somers et al., 2019).

200 <u>To further discuss the role of low flow in F^*_{yw} estimation, let's first consider that F^*_{yw} can be estimated based on the flowweighted average of young water fractions (Kirchner, 2016b):</u>

$$F_{yw}^{*} = \frac{A_{S}^{*}}{A_{P}} \simeq \frac{\sum_{i=1}^{n} Q(t_{i}) F_{yw}(t_{i})}{\sum_{i=1}^{n} Q(t_{i})},$$

(1)

where n is the number of time-steps (e.g., days) in the period of isotope sampling, PoS, $Q(t_i)$ is the discharge at the time t_i (e.g., daily discharge), $F_{yw}(t_i)$ is the young water fraction at the time t_i (e.g., daily young water fraction). As is clear from Eq. 205 (1), F_{yw}^* becomes low if either $F_{yw}(t_i)$ is low for high flows or if $F_{yw}(t_i)$ is very low for many time steps or both. The lowflow periods correspond to the recession periods in which there is no new rainfall or meltwater input in the catchments. Thus, during these periods, the catchment storage releases stored water (or old water) to the stream sustaining the streamflow (Hayashi, 2020). Thus, we can anticipate that low $Q(t_i)$ values imply low $F_{yy}(t_i)$ values. Accordingly, the proportion of the low-flow period during a specified time-window should reduce the amount of young water reaching the stream during that 210 time-window. Nevertheless, the $F_{vw}(t_i)$ is higher during high flow (wet) periods (von Freyberg et al., 2018; Wilusz et al., 2017; Gallart et al., 2020b). Thus, the overall effect of the proportion of low-flow and high-flow periods upon F^*_{yw} remains a priori unclear. It is however tempting to think that the duration of low-flow period or the share of baseflow could explain F^*_{vv} changes at different elevations (since both low-flow duration and the share of baseflow change with elevation). In addition, in high-elevation, snow-dominated catchments the snowpack persistence is the main driver of low-flow duration, 215 since the low-flow period in such environments corresponds to the presence of the seasonal snowpack (corresponding to an absence of liquid water input), while the high-flow period is generally snowmelt-driven. Such snowmelt generally occurs in late spring or summer and it is likely to be older than 2-3 months (because melted snow fell more than 3 months before the onset of snowmelt). As a result, summer discharge would mainly consist of old water: either of current snowmelt that reaches the stream via faster surface or subsurface flow paths or old snowmelt (main component of groundwater storage) 220 pushed out in the stream by infiltrated rainwater or meltwater. Of course, part of the snowpack could release young water, but this should be a minor component in catchments with a seasonal snowpack. In contrast, in catchments with an ephemeral snowpack, it is common to observe intermittent winter snowmelt that is likely younger than 2-3 months: snowmelt is

- temporally close to snowfall. In this case streamflow receives relatively more young water from short-lived snowpacks. However, it is still unclear if seasonal or ephemeral snow cover dynamics can affect the F*_{yw} (Ceperley et al., 2020).
 A special focus of our work is on variables that were not previously considered for explaining elevation gradients of young
- water fractions. We namely exclude catchment size, annual precipitation, bedrock porosity, pasture cover, open water cover that have been discussed and shown to have little correlation in the work of Jasechko et al. (2016).

<u>A special case in terms of explanatory variables is mean annual precipitation:</u> Jasechko et al. (2016) in their worldwide study did not observe any significant correlation between the F^*_{yw} and annual precipitation. Lutz et al. (2018) found, based on 24

- 230 catchments in Germany, that F^*_{yw} decreases with increasing mean annual precipitation. In contrast, in the relatively wet rainfall-dominated and hybrid catchments studied by von Freyberg et al. (2018), F^*_{yw} was shown to increase with precipitation, which in turn both increase with elevation. In their study, discharge (unsurprisingly correlated with precipitation) was considered as a proxy of catchment wetness, which favours rapid flow paths and thereby increases F^*_{yw} (von Freyberg et al., 2018). In snow-dominated systems, the use of mean annual precipitation as a proxy for catchment
- 235 wetness could be misleading because the seasonal snowpack leads to a very dry period of the year despite the high *solid* water input. In other words, the temporal concentration of the liquid water input is the relevant variable. Indeed, the saturation of the system (i.e., high wetness conditions) can be observed also when the annual precipitation is low if a large volume of water (stored in the snowpack) is released in a relatively concentrated time interval. Indeed, despite precipitations, and correspondingly discharges, are relatively higher in snow-dominated than in rainfall-dominated
- 240 catchments, F^*_{yw} is generally lower in snow-dominated systems that are potentially wetter than rainfall-dominated ones. This suggests that the only precipitation can only partially explain the variations of F^*_{yw} and that other variables should be put under observation.

Accordingly, we omit here total annual precipitation as explanatory variable of low F^*_{yw} in snow-dominated catchments (but we consider precipitation for rainfall-dominated and hybrid catchments) and study a new set of hydrological variables to

245 gain new insights into F*_{yw} along elevation gradients: the fraction of Quaternary deposits (F_{qd}), the average fraction of baseflow (F_{bf}), the low-flow duration (LFD) and the average fractional snow cover area (F_{SCd}), defined in detail in Section 3.2 and Section 3.3. In the following, we first describe the data set (Section 2). Then, we present the correlation analysis of the selected hydrological variables with F*_{yw} and we bring these results back into the ongoing scientific discussion of F*_{yw} (Sections 4.1, 4.2, 4.3, 4.4, 4.5).

250 2 Study sites

In this work weWe analyze– 27 study catchments located both in Switzerland and Italy (Table S1, Fig. 1) and integrateintegrating observations from multiple published existing datasets<u>data sets</u> (25 catchments) with new additional observations (2 catchments).) (Fig. 1). Geomorphological and hydro-climatic characteristics of the study sites are reported in Table 1.

255 2.1 Existing dataset

Initial, we integrate the 22 Swiss catchments studied by von Freyberg et al. (2018) with the three Alpine catchments (Vallon de Nant, Noce Bianco at Pian Venezia and Bridge Creek Catchment) investigated by Ceperley et al. We assembled the 22 Swiss catchments studied by von Freyberg et al. (2018) with the three alpine catchments investigated by Ceperley et al. (2020) into a single dataset. Time series of both δ^2 H and δ^{140} O in streamflow and precipitation for the 22 Swiss catchments are reported and described by Staudinger et al. (2020). Furthermore, 21 out of the 22 Swiss catchments were also considered

in a previous study (which did not consider the Alp catchment) that analyzed the variation of the catchment water storage with elevation (Staudinger et al., 2017). In turn, daily isotope measurements for the Alp (ALP) catchment and its two tributaries, Erlenbach (ERL) and Vogelbach (VOG) catchments, were thoroughly described by von Freyberg et al. (2022). Two high elevation catchments among the 22, namely Dischmabach (DIS) and Ova da Cluozza (OVA), were also investigated in previous studies for climate change impact predictions, low flow analysis and for understanding the role of

- quaternary deposits and groundwater in their hydrological functioning (Addor et al., 2014; Staudinger and Seibert, 2014; Staudinger et al., 2015; Jenicek et al., 2018; Arnoux et al., 2021). Among the catchments analyzed by Ceperley et al. (2020), the reader is referred to Michelon et al. (2022) for further information about the tracer-based dynamics of the Vallon de Nant (VdN) catchment and to Carturan (2016), Carturan et al. (2013, 2014, 2016, 2019), Zuecco et al. (2019) for glaciological, hydrological and meteorological information about the Noce Bianco at Pian Venezia (NBPV) catchment. Additional details
- for the dolomitic Bridge Creek Catchment (BCC) are available in the work of Zuecco et al. (2018, 2019), Guastini et al. (2019) and Penna et al. (2016, 2017).

2.2 Additional dataset

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We consider two additional high elevation catchments located near the Nivolet Pass (Valsavaranche, Aosta Valley, Italy) in 275 a high-elevation grassland within the Gran Paradiso National Park territory (Gisolo et al., 2022). The mainstream is the Dora del Nivolet. Hereafter we refer to this catchment simply as "Dora" (DOR). DOR has a catchment area of 17 km² and its elevation ranges from 2390 to 3430 m a.s.l. Average annual precipitation in the period 2017-2021 was 2164 mm. It experiences a snow-dominated hydro-climatic regime with the snowpack generally persisting from mid-November to mid-May when the snowmelt starts. Since the snowpack melts during the growing season, it uncovers a typical alpine meadow home to plant species including Gentiana Lutea L., Juniperus Communis L., Vaccinium Myrtillus L., Salix Alpina Scop. and 280 Trifolium Alpinum L. The lithology of DOR is dominated by gneiss. Bedrock emerges at high elevations, while at medium elevations the talus dominates. At lower elevations we find the alpine meadow, characterized by peat substrate, through which the mainstream flows. We monitor precipitation every month with a rain gauge located at roughly 2560 m a.s.l. We measure streamflow continuously (10 min timestep) at the DOR outlet point and in a lateral subcatchment, on the left bank 285 of the mainstream, using piezo-resistive multi-sensors. We call this lateral subcatchment "Source" (SOU), since it is eharacterized by water emerging from underground. The SOU subcatchment extends for roughly 0.16 km² and its elevation ranges from 2390 to 2790 m a.s.l. Water samples for isotopic analysis are collected of both bulk precipitation and streamwater at a monthly time resolution. Specifically, precipitation samples were collected using a double rain and snowfall isotope sampler installed on a pole 3.7 m high, near the rain gauge, while streamwater was sampled manually (Fig. S1). All 290 precipitation and streamwater samples were analyzed with laser spectroscopy at the Forest Hydrology laboratory of University of Padova.

2.3 Complete dataset

The von Freyberg et al. (2018) dataset includes catchments with areas between 0.7 and 351 km² and mean elevations between 472 and 2369 m a.s.l. Average annual precipitation in these catchments ranges from 887 to 2615 mm. With the data

295 added here, the entire dataset now covers areas between 0.14 and 351 km² and has mean elevations between 472 and 3049 m a.s.l. Specifically, the additional 5 catchments added to the initial dataset of von Freyberg et al. (2018) allow analysis to explore the high elevation (i.e., > 1500 m a.s.l.) regions that were previously poorly represented. Furthermore, the complete dataset now includes case studies from five different Alpine regions, including the Northern part of the Swiss Alps, the Southern Swiss Alps (Alpi Ticinesi), the Western Italian Alpes (Alpi Graie), the Rätische Alpen and the Dolomites. This represents a good range of geologies as well as of climatic conditions, as visible from Table 1.

Like von Freyberg et al. (2018), we classify the catchments in the three hydro-climatic regimes (snow-dominated, hybrid and rainfall-dominated) proposed by Staudinger et al. (2017), but we introduce a new formal criterion of classification (see Section 3.3).

The geographical framework of the selected catchments is illustrated in Fig. 1 and their geomorphological and climatic 305 characteristics are reported in Table 1.



(Vallon de Nant, Noce Bianco at Pian Venezia and Bridge Creek Catchment) into a single data set. Hereafter we refer to these catchments with the ID reported in the above-mentioned published papers (Table 1). We also consider two additional high-elevation catchments located near the Nivolet Pass (Valsavaranche, Aosta Valley, Italy) (Gisolo et al., 2022). In this Alpine environment, we monitor the mainstream, called "Dora del Nivolet", and a secondary river called "Source". Hereafter

10

we refer to these catchments with the ID: DOR and SOU, respectively. A detailed description of the DOR and SOU catchments is reported in the Supplementary Material.

- The von Freyberg et al. (2018) data set includes catchments with areas between 0.7 and 351 km² and mean elevations between 472 and 2369 m a.s.l. With the five catchments added here, the complete data set covers areas between 0.14 km² and 359 km² and has mean elevations between 472 and 3049 m a.s.l. The average precipitation is comprised between 61.3 mm month⁻¹ and 168.7 mm month⁻¹ while mean discharge is comprised between 28.6 mm month⁻¹ and 138.9 mm month⁻¹. The average slope ranges from 4° to 34°, and our study sites reveal an increase of steepness with elevation (Fig.2a, Fig.2b). Precipitation increases with elevation until 1500 m a.s.l. and it decreases for higher elevations (Fig. 2c, Fig. 2d), highlighting
- 320 a change of precipitation regime as described by previous studies (Santos et al., 2018). The five catchments added to the initial data set of von Freyberg et al. (2018) allow the analysis to explore the high-elevation regions (average elevation > 1500 m a.s.l.) that were previously poorly represented. Most of the study catchments reveal a sedimentary bedrock, but also dolomitic and metamorphic bedrocks, characteristic of high-elevation sites, are included in our data set. Moreover, the presence of unconsolidated Quaternary deposits is widespread among our study catchments: only two catchments (BCC and
- 325 SOU) do not reveal this type of geology. The complete data set now explores case studies from the Swiss plateau and Prealpine area, from the Jura and from five different Alpine regions, including the Northern part of the Swiss Alps, the Southern Swiss Alps (Alpi Ticinesi), the Western Italian Alps (Alpi Graie), the Rätische Alps and the Dolomites. In summary, this represents a good range of geologies as well as of climatic conditions.
- In order to be consistent with previous studies (von Freyberg et al., 2018; Staudinger et al., 2017), we classify the 23 Swiss catchments according to the hydro-climatic regimes proposed by Staudinger et al. (2017) which group the regimes defined by Weingartner and Aschwanden (1992) in three categories: rainfall-dominated (R), hybrid (H) and snow-dominated (S). For the four Italian catchments, where the aforementioned classification schemes cannot be rigorously applied, we use that proposed by Stoelzle et al. (2020). This classification scheme is based on mean and maximum catchment elevation, periods of typical low-flow, snow onset and begin of snowmelt and was already used by Stoelzle et al. (2020) to classify catchments
- 335 outside the Swiss borders (e.g., German catchments). According to this classification scheme, the four Italian catchments (DOR, SOU, BCC and NBPV) are all categorized as snow-dominated (S). The classification of BCC is also consistent with the one given in a previous study without considering the application of a formal classification scheme (Penna et al., 2016). Across the three considered streamflow regimes, a shift of the monthly hydrograph peak (computed using discharge data in the PoS) from winter to summer months is observed (Fig. 3): this "flow peak-shifting" is a clear sign of the increasing
- 340 predominance of snowmelt in the streamflow generation processes. Our data set includes NBPV, whose area is 42% glaciercovered and consequently shows a characteristic glacier-dominated streamflow regime with a monthly peak in late summer. Thus, NBPV may belong to a fourth category of glacier-dominated catchments, for which the effect of glacier-melt on F*_{yw} cannot be neglected, and this was partially discussed by Ceperley et al. (2020). In our data set, also the Dischmabach (DIS)





Figure 4.1 Location of the 27 study catchments with indication of hydro-elimatic regime and quaternary deposits coverage discussed in Section 4.2 and Section 4.3.2. the hydro-elimatic regime.

350 Table 1. Catchments geomorphological and climatic characteristics. Catchments area and average slope are directly calculated in Google Earth Engine. For the slope calculation we use the Shuttle Radar Topography Mission (SRTM) DEM. We obtained elevation and annual precipitation information of the existing dataset directly from published papers (Staudinger et al., 2017; von Freyberg et al., 2018; Ceperley et al., 2020).



Figure 3 Boxplots of mean monthly flow for all the study catchments grouped according to their flow-regime (rainfall-dominated, hybrid, snow-dominated). Coloured areas represent the monthly flow of each study catchment belonging to the relative regime.

 Table 1 Catchments geomorphological and hydro-climatic characteristics. Catchments area and average slope are directly calculated in Google Earth Engine. For the slope calculation we use the Shuttle Radar Topography Mission (SRTM) DEM (Farr et al., 2007). We obtained average elevation and precipitation information of the existing data set directly from published papers (von Frevberg et al., 2018; Ceperley et al., 2020). Discharge (O), Precipitation (P) and isotopic composition (δ¹⁸O) data are all referred to the Period of Sampling (PoS) indicated in this Table. The letter in brackets in the first column indicates the hydro-climatic regime; (R) = Rainfall-dominated, (H) = Hybrid, (S) = Snow-dominated.

ID <u>(Regime</u> <u>)</u>	Area (km²)	Avera _t Elevation	ge <u>Avg</u> (m a.s.l.)	min Elevation (m a.s.l.) <u>ran</u> <u>ge (min-</u> <u>max)</u>	max Elevatio n (m a.s.l.)	Aver age <u>A</u> vg Slop e (°)	Dominant geology	Annual Prec. Monthl y P (mm month 1)	Monthl vQ (mm month 1)	<u>PoS</u> δ ¹⁸ Ο, Ο, Ρ	Celle eliminate Celle inserite Celle inserite
AAB (R)	46.07	635	<u>517</u>	<u>519-</u> 1	092	5.73	Rock (upper freshwater molasse)Sedim entary Rock	<u>1081106</u> <u>.1</u>	<u>56.48</u>	<u>Sep 2010-Feb</u> 2013	Celle eliminate
AAC (R)	47.25	47	2	408 <u>-560</u>	<u>560</u>	4.02	Unconsolidated sediments (moraine)	1095 <u>85.</u> <u>1</u>	<u>35.73</u>	Jul 2010-Dec 2011	Celle eliminate
ALL <u>(S)</u>	28.71	1852		1293 <u>-</u> <u>2742</u>	2742	25.48	Sediment.Scdi mentary Rock and unconsolidated sediments (flyseh, sandstones, profound weathering soils, avalanche debris, hanging rubble and cones of dry rubble)	1651<u>99.</u> 4	118.04	<u>Sep 2010-May.</u> 2015	

			845				Sediment.Sedi				 Celle eliminate
ALP (<u>H</u>)	46.59	1154		<u>845-</u> 18	94	16.50	mentary Rock and unconsolidated sediments (flyseh, conglomerate s, sandstones, marls, earbonate- rich molasse, alluvions)	<u>2112158</u> .2	<u>123.52</u>	<u>May 2010-Dec</u> 2015	
BCC (S)	0.14	21	21	1932 <u>-</u>	2515	22.88	Dolomite	<u>1203100</u>	111.83	Mar 2010-Oct	 Celle eliminate
BCC <u>(5)</u>	0.14	21.	21	<u>2515</u>		22.00	Doioinite	<u>.3</u>	111.05	<u>2017</u>	
BIB <u>(R)</u>	31.83	999	<u>827</u>	<u>827-</u> 14	95	12.43	Sediment_Scdi mentary Rock and unconsolidated sediments (conglomerat es; sandstones; marls; carbonate- rich molasse; Grindelegg- series; granitic molasse; Torfmoor; alluvions; moraine)	1 63 9 <u>150</u> .2	<u>94.78</u>	<u>May 2010-Nov</u> 2015	Celle eliminate

DIS <u>(S)</u>	42.75	230	59	1663 <u>-</u> <u>3139</u>		26.28	Metamorphic rock (metagranitoi ds, amphibolites, mica shist, gneiss, moraine)	1391 <u>76.</u> <u>4</u>	<u>108.11</u>	<u>Nov 2010-May</u> 2015	Celle eliminate
DOR (S)	16.99	27	11	2390 <u>-</u> <u>3430</u>	3430	19.37	Metamorphic rock-(gneiss, amphibolites, alluvions)	2164<u>147</u> <u>.4</u>	<u>107.79</u>	<u>Nov 2017-Jan</u> 2022	
ЕММ (<u>H)</u>	124.0 3	1285	743	743-2	2216	19.71	Sediment. Rock (mediterranea n molasse, subalpine molasse, ground lime formation, calcareous quartz sandstone, moraine, hanging rubble, cone of dry rubble)Scdime ntary Rock	1559<u>116</u> .6	<u>91.99</u>	<u>Jun 2010-Nov</u> 2013	Celle eliminate

ERG (R)	260.4 7	584	305	<u>305-</u> 1	.165	13.86	Sediment. Rock (conglomerat e, sandstone, subordinately siltstone, marl, crust limestone, oolitie, peloidal and micritie limestone, Staffelegg- formation, Opalinus- Ton,scree)Scdi mentary Rock	1012<u>87.</u> 7	<u>37.88</u>	<u>Jun 2010-Nov</u> 2015	
ERL (<u>H)</u>	0.74	13	59	1117 <u>-</u> <u>1650</u>	,1650	13.53	Sediment.Sedi mentary Rock (flysch, eboulis)	<u>2168162</u> <u>.4</u>	<u>138.04</u>	<u>Jul 2010-May</u> 2015	Celle eliminate
GUE (H)	55.23	1037	<u>_556</u>	<u>556-</u> 2152		16.84	Sediment.Sedi mentary Rock and unconsolidated sediments (flyseh, eboulis, dry eones, Sequanian, moraine)	<u>124194.</u> 2	77.69	<u>Jul 2010-Dec</u> 2012	Celle eliminate

ILF <u>(H)</u>	186.9 4	1037	681	<u>681-</u> 2087	19.36	Sediment. Rock (colorful polymictic conglomerate subordinate to sandstone and marl or silty marl, mediterranean molasse, flysch subalpine, alluvions)Sedi	<u>1450127</u> . <u>5</u>	81.09	Jul 2010-May 2015
AN D	59.76	760	598	<u>598-</u> 1100	10.08	subalpine, alluvions)Scdi mentary Rock Sediment. Rock (Napf formation and St. Gallen formation under thin quaternary eover, Dürrenroth gravel, alluvions)Scdi	+++95 <u>118</u> _2	54.78	Jul 2010-May 2015
LUM (<u>H)</u>	1.20	13	36	1092 <u>-</u> <u>1508</u>	12.49	mentary Rock Sediment-Sedi mentary Rock (flysch)	<u>2615157</u> <u>.1</u>	<u>113.63</u>	Oct 2010-Nov 2015

MEN (<u>R)</u>	105.0	61	79	447 <u>-926</u>	926	6.19	Sediment.Scdi mentary Rock and unconsolidated sediments (variegated sandstone and marl under thin morainie cover, sandstone and marl, moraine)	1060<u>89.</u> 3	<u>28.64</u>	Jul 2010-Feb 2013	
MUR (R)	79.92	648	<u>467</u>	<u>467-</u> 1	.036	10.52	Sediment-Scdi mentary Rock and unconsolidated sediments (upper freshwater molasse, moraine, postglacial gravel)	<u>+281116</u> . <u>6</u>	<u>60.57</u>	<u>Jul 2010-Nov</u> 2014	Celle eliminate
NBPV (<u>S)</u>	8.39	3049		2298 <u>-</u> <u>3769</u>	<u>3769</u>	23.27	Metamorphic and sediment. <u>sedi</u> <u>mentary</u> rock (phyllites, paragneiss, parascists)	<u>1413117</u> <u>.8</u>	<u>137.80</u>	<u>May 2013-Sep</u> 2015	Celle eliminate
OVA (<u>S)</u>	26.87	2364		1519 <u>-</u> <u>3160</u>	3160	32.73	Dolomite	<u>88761.3</u>	73.21	<u>Aug 2010-Sep</u> 2013	

									-		
RIA <u>(S)</u>	23.85	1986	<u>881</u>	<u>881-</u> 2	908	32.93	Metamorphic rock (Biotite, granodiorite, gneiss, mica shist, hanging rubble and cones of dry rubble)	<u>2104129</u> <u>.3</u>	<u>143.49</u>	<u>Jul 2010-Dec</u> <u>2012</u>	Celle eliminate
RIE <u>(R)</u>	3.18	79	4	671 <u>-938</u>	<u>938</u>	13.23	Sediment.Scdi mentary Rock and unconsolidated sediments (upper freshwater molasse, moraine)	1555<u>121</u> .<u>1</u>	<u>85.58</u>	<u>Jul 2010-Feb</u> <u>2013</u>	Celle eliminate
SCH <u>(S)</u>	107.6 1	1719	<u>487</u>	<u>487-</u> 3	260	28.78	Sediment-Scdi mentary Rock and unconsolidated sediments (flysch, settling mass, rockslide, moraine)	<u>1687140</u> <u>.0</u>	138.93	<u>Apr 2011-May</u> 2015	Celle eliminate
SEN (<u>H</u>)	350.2 4	1068	554	<u>554-</u> 2	184	15.35	Sediment. Rock (flysch, sandstone, marls, seists, moraine)Sedim entary Rock	1270 <u>95.</u> 2	53.66	<u>Oct 2010-Mar</u> 2013	

SIT <u>(H)</u>	74.23	1301	768	<u>768-2</u> .	500	22.15	Sediment. Rock (lower freshwater molasse; Helvetian calcareous limestone; lower Sehrattenkalk; moraine)Sedim entary Bock	<u>1870168</u> <u>.7</u>	<u>115.47</u>	<u>Nov 2010-May</u> 2015	
SOU <u>(S)</u>	0.16	26	36	2390 <u>-</u> 2790	2790	25.74	Metamorphic rock (gneiss)	<u>2164147</u> <u>.4</u>	<u>64.47</u>	Nov 2017-Jan 2022	Celle eliminate
VdN <u>(S)</u>	13.55	19	66	1189 <u>-</u> <u>3051</u>	3051	34.00	Sediment. Rock (flysch, sandstone, marls)Sediment ary Rock	<u>1591132</u> <u>.6</u>	<u>99.14</u>	<u>Nov 2015-Dec</u> 2018	
VOG (<u>H</u>)	1.57	13	35	1038 <u>-</u> <u>1540</u>	1540	18.42	Sediment. <u>Sedi</u> mentary Rock (flysch)	<u>2161162</u> <u>.2</u>	<u>120.24</u>	<u>Jun 2010-Nov</u> 2015	

3 Material and Methods

3.1 Discharge data and catchments boundaries

Daily discharge data for the Erlenbach (ERL), Lümpenenbach (LÜM) and Vogelbach (VOG) catchments are provided by the *Swiss Federal Institute for Forest, Snow and Landscape research (WSL)*, Birmensdorf, Switzerland. Moreover, streamflow
data for the Aabach (AAB) and Guerbe (GUE) catchments are provided by the *Office for Waste, Water, Energy and Air* (*WWEA*) of the Canton of Zurich and by the *Office for Water and Waste* of the Canton of Bern, respectively. Vallon de Nant (VdN) 1-min discharge measurements are obtained via an optical height gauge above the middle point of a trapezoid shape weir (Antoniazza et al., 2022; Michelon et al., 2022), and they are subsequently aggregated to daily streamflow values. Bridge Creek Catchment (BCC) and Noce Bianco at Pian Venezia (NBPV) catchment daily streamflow data are provided by
Dr. Giulia Zuceco, (University of Padova, Italy). Daily discharge data for the DOR and SOU catchments are obtained aggregating 10 min measurements deriving from piezo resistive multi-sensors (as described in Section 2). Daily discharge

data of the remaining 17 Swiss catchments studied by von Freyberg et al. (2018) are provided by the Swiss Federal Office for the Environment (FOEN).

We obtain the .shp of the AAB, GUE, ERL, LÜM and VOG catchments boundaries from the Zenodo data repository
 reported in Staudinger et al. (2020); the .shp of NBPV, BCC and VdN catchments, are provided by Dr. Giulia Zucceo and Dr. Anthony Michelon (University of Lausanne, Switzerland) as personal communication. We delineate the DOR and SOU catchments boundaries in a GIS environment using the 10-m resolution Digital Elevation Model (DEM) available from the *Aosta Valley Regional Geoportal*. Finally, we obtain the catchment boundaries of the remaining 17 Swiss catchments investigated by von Freyberg et al. (2018) directly from the *Swiss Federal Office for the Environment (FOEN)*.

390 3.2<u>3.1</u> Young water fraction estimation from seasonal cycles of stable water isotopes in precipitation and streamwater: the "direct" input.

Kirchner (2016a) has demonstrated that the F_{juu} young water fraction can be easily approximated accurately predicted by the amplitude ratios of seasonal sine curves fitted to streamwaterstream water and precipitation isotope values. Operatively, seasonal isotope (e.g., δ^{18} O) cycles in streamwaterstream water and precipitation can be modelled by:

395	$\delta^{18}O_S(t) = A_S \sin(2\pi f t - \varphi_S) + k_S ,$		(1)
		(2)	
	$\delta^{18}O_P(t) = A_P \sin(2\pi f t - \varphi_P) + k_P ,$		-(2),
		(3)	

where, $\delta^{I8}O$ (‰) is the isotopic composition of water sampled at the time *t* (expressed in decimal years), *A* (‰) is the amplitude of the seasonal isotope cycle, φ (in radians) is the phase, *f* (yr⁻¹) is the frequency and *k* (‰) is the vertical offset of the seasonal isotope cycle. The subscript "S" refers to streamwater, while the subscript "P" refers to precipitation. As in the work of Kirchner (2016a), we fit the sine curves of Eq. (1) and Eq. (2) on the isotope measurements using the *Iteratively Reweighted Least Squares (IRLS)* method (for reducing the influence of outliers) and then estimate the *A*, φ and *k* parameters.

stream water, while the subscript "P" refers to precipitation. As in the work of von Freyberg et al. (2018), the sine curves of
Eq. (2) and Eq. (3) can be fitted on the isotope measurements (using the *Iteratively Re-weighted Least Squares* method for reducing the influence of outliers), which leads to estimates of A, φ and k parameters. The sine wave is fitted to the isotopes measured in precipitation weighted according to the volume of precipitation to reduce the influence of low-precipitation periods and to account for temporally aggregated rainfall samples (von Freyberg et al., 2018); the sine-fit of stream water isotope measurements can be discharge-weighted or not, using the discharge measured at the moment of sampling as weights
(von Freyberg et al., 2018). Consequently, an unweighted amplitude (A_S) or a flow-weighted amplitude (A*_S) can be obtained. Thus, following Kirchner (2016a), it is possible to calculate the time-weighted or flow-weighted young water fractions (F_{yw} or F*_{yw}) via the "amplitude ratio approach":

$F_{mn} = \frac{A_S}{M_S}$	(*
$Y_{yw} = A_P$.	(-
	(4.1)

- 415 We fit a sine wave to the isotopes measured in precipitation according to volume of precipitation to reduce the influence of low-precipitation periods and to account for temporally aggregated rainfall samples (von Freyberg et al., 2018); the sine-fit of streamwater isotope measurements can be discharge-weighted or not, using the discharge measured at the moment of sampling as weights (von Freyberg et al., 2018). Consequently, we obtain an unweighted A_S or a flow-weighted A_S with which Eq. (3) can be evaluated. The uncertainty of these estimated F_{yw} (flow-weighted or unweighted) are calculated using the Gaussian error propagation (von Freyberg et al., 2018). Flow weighting was used in both the work of von Freyberg et al. (2018) and Ceperley et al. (2020). Gallart et al. (2020) highlighted the advantages of the flow-weighted analysis (generally yielding flow-weighted A_S greater than unweighted A_S) to compensate for subsampled high-flow periods. Thereby, for the existing dataset, we consider the values of flow-weighted F_{yw}-reported in Table 3 of von Freyberg et al. (2018) and in Table 6 of Ceperley et al. (2020) with associated errors.
- 425 Accordingly, for the additional dataset composed by the DOR and SOU catchments, we apply the procedure above for calculating the flow-weighted F_{yw} using δ^{18} O measurements collected in the period November 2017 January 2022.

3.3 A new hydro-climatic regime classification: the classifiers

Our analysis focuses on Alpine catchments whose streamflow regimes are dominated by natural precipitation runoff transformation processes. The corresponding streamflow regimes are classically divided into those that are rainfall-driven
 (often called pluvial) and those that are snow dominated, with or without glacier influence and possibly including hybrid regimes (Weingartner and Aschwanden, 1992; Moore et al., 2012; Staudinger et al., 2017).

While the streamflow regime terminology is omnipresent in hydrology literature, there is often no formal classification method provided (Déry et al., 2009). Switzerland has a formal streamflow regime classification into 16 regimes, largely based on Pardé coefficients (Pardè, 1933), i.e. monthly streamflow ratios (Weingartner and Aschwanden, 1992), used by a

435 few additional authors (Curran and Biles, 2021). Some authors consider mean catchment elevation or human influence (Piccolroaz et al., 2016). These classifications are typically based on streamflow data and some topographical data (e.g., elevation and glacier cover).

We design a new criterion, explained below, for classifying streamflow regimes as rainfall-dominated, hybrid and snowdominated, which should be as parsimonious as possible (i.e., using few explicative variables) and account explicitly for the

440 snow cover regime in the catchments. As a proxy for the snow cover regime, we use the average fractional Snow Cover Area (F_{SC4}): we discuss its computation in Section 3.4. Staudinger et al. (2017) classify the catchments in the above-mentioned clusters grouping some of the regimes defined by Weingartner and Aschwanden (1992) that are built on the streamflow regime in Switzerland. The tricky points of this "three regimes classification" are the transitions, both from rainfall-

dominated to hybrid catchments and, similarly, from hybrid to snow-dominated ones. Focusing on these transitions, in both cases, we reason that the role of snowpack is crucial. From our knowledge of the regime classification systems already existing in literature, there are no studies that explicitly consider the role of snow. Expansion in satellite data ubiquity, frequency, and accessibility has rendered the assessment of snow cover only recently feasible.

For the classification, we further use a common monthly streamflow ratio, namely the Q_{lum}/Q_{DM}-ratio (i.e., ratio of the average flow of June and the sum of average flow of December, January, and February), as a classifier. Flow is relative to catchment area; it is expressed in mm per time step. Using the regime classification of Staudinger et al. (2017) as a base, we compare the monthly streamflow of their catchments belonging to different regimes and we focus thereby on Q_{DM}- (as proxy for winter flow) and Q_{Jum} (as a proxy for summer flow). It is in fact during these two periods that Q_{Jum} and Q_{DM}- different regime types, as shown in Fig. 2. Accordingly, our new classification scheme (Section 4.2) is based on two variables: the F_{SC4} and Q_{Jum}/Q_{DM}- ratio.



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460

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Figure 2. Boxplots of mean monthly flow for catchments studied by Staudinger et al. (2017) and grouped according to their flowregime classification (rainfall-dominated, hybrid, snow-dominated)

3.4 Average fractional Snow Cover Area (FSCA) computation

The F_{SCA} for each catchment is calculated over the period October 1st 2017– September 30th 2021 (hereafter defined as PoI,

i.e., Period of Interest) starting from $F_{yw}^* = \frac{A_S^*}{A_P^*}$

(4.2)

Gallart et al. (2020a) highlighted the advantages of the flow-weighted analysis (generally yielding A_{s} greater than A_s) to compensate for subsampled high-flow periods, which would otherwise lead to a young water fraction underestimate. Accordingly, we will consider in this work, for all the study catchments, only the flow-weighted young water fractions. The uncertainty of these estimated F_{syn}^* can be obtained using a Gaussian error propagation (von Freyberg et al., 2018).

The analytical choice of using the amplitude (A_P) fitted on precipitation isotopes, instead of the amplitude (A_{Peq}) fitted on the equivalent precipitation (i.e., rain + snowmelt) isotopes, for estimating F^*_{yw} implies that the snowpack is considered as part of the catchment storage and that the damped seasonal cycle observed in the stream is given by the mixing of precipitation with snowpack and subsurface storage (the last two considered as a single entity), as illustrated in Fig. 4:



Figure 4 Schematic representation of the "direct input" approach for estimating F^*_{pm} . Light blue arrows indicate that meltwater
coming from the snowpack preferentially infiltrates. The term "C" refers to the isotopic composition. The subscripts: "P" refers
to "Precipitation", "S" refers to "Stream", "SP" refers to "Snowpack", "Sub" refers to "Subsurface storage" and "St" refers to
"Catchment storage".475

For the published data sets (von Freyberg et al., 2018; Ceperley et al., 2020), we consider the F^*_{yw} values, with associated errors, published or provided by the authors, while for the DOR and SOU catchments we estimate F^*_{yw} applying the methodology described in this Section (more info are available in the Supplementary Material). A plot of F^*_{yw} against mean elevation for the 27 study sites is shown in Fig. 5. F^*_{yw} values for all the study catchments are reported in Table 2.

480



Figure 5 F*_{yw} as function of mean catchment elevation.

3.2 Snow cover persistence quantified through the average fractional snow cover area (Fsca)

In this paper, we quantify the snowpack persistence calculating the average fractional Snow Cover Area (F_{SCA}). It is calculated, for each catchment, over the period October 1st, 2017- September 30th, 2021 (hereafter defined as PoC, i.e., period of calculation) using Sentinel-2 L2A satellite images. Temporally, this relatively recent satellite has increased the visitation frequency to more than a sub-weekly temporal resolution and increased the spatial resolution to 20 m for snow cover (Gascoin et al., 2019). High temporal resolution makes Sentinel-2 images preferable to Landsat images, which are available only once every 16 days and whose total number is often further reduced because of cloudiness (Hofmeister et al., 2022). The PoC generally differs from the PoS for the 27 study catchments. This is because Sentinel-2 L2A satellite images are not available before March 2017. For each image available in the PofPoC, we calculate the Normalized-Difference Snow Index (NDSI) as suggested in the work of Dozier (1989):
NDSI: = ^{#green+#5WIR}/_{#green+#5WIR} (4)

495 NDSI = $\frac{r_{green} - r_{SWIR}}{r_{green} + r_{SWIR}}$

500

(5)

where r_{green} is the reflectance in the green band (Sentinel-2 band 3) and r_{SWIR} is the shortwave infrared reflectance band (Sentinel-2 band 11). We classify as snowy pixels those with a NDSI value > 0.4 (Dozier, 1989). Based on the pixel-wise snow classification, we compute f_{SC4} as in the works of Di Marco et al. (2020) and Hofmeister et al.Based on the pixel-wise snow classification, we compute the snapshot fractional Snow Cover Area (f_{SC4}) as in the works of Di Marco et al. (2020) and Hofmeister et al. (2022):

f Nsnow	(5	<u>)</u>
JSCA - Ntot-Nclouds	(5	7
	(6)	

where N_{snow} is the number of snow cover <u>pixelpixels</u> according to the applied NDSI threshold method, N_{tot} is the total number of pixels within the catchment area and N_{clouds} is the number of pixels classified as <u>eloudclouds</u> and water bodies
 (Hofmeister et al., 2022). We identify the cloudy pixels directly using the Sentinel 2 band "Scene Classification Map". We operatively calculate N_{snow}, N_{tot} and N_{clouds} using a Google Earth Engine script.

. We identify the cloudy pixels directly using the Sentinel-2 band "Scene Classification Map". We operatively calculate *N_{snow}*, *N_{tat}* and *N_{clouds}* using a Google Earth Engine (Gorelick et al., 2017) script.

- Using this procedure for calculating f_{SC4} , we sometimes obtain $f_{SC4} > 1$, typically for winter satellite images. The NDSI threshold method is generally able to distinguish between snow and no-snow pixels (Aalstad et al., 2020). Accordingly, clouds and snow have similar reflectance in the green band, but clouds highly reflect in the shortwave infrared band, while snow reflectance is low in this band. Thus, the N_{snow} estimation is generally accurate. On the other hand, it is necessary to reducenot consider the number of false positive pixels deriving from clouds detection (i.e., snow classified as clouds).
- During winter itlf $f_{SC4} > 1$, we calculate f_{SCA} as N_{snew}/N_{tot} since this is likely the only heuristic solution that N_{snow} -approaches very close to N_{tot} -Accordingly, it is easy to have $N_{tot}-N_{clouds} < N_{snow}$ if N_{clouds} incorporate pixels that are in fact snow covered. In these cases, we assume that $N_{clouds} = N_{tot}-N_{snow}$ (i.e., $f_{SC4}=1$).guarantees no overestimation. Moreover, by looking at sample Sentinel-2 images during the summer periods for all the catchments, we impose $f_{SC4} = 0$ during July and August, since when f_{SC4} other than $\neq 0$ -has, this usually results from falsely identified clouds as snow; imposing $f_{SC4} = 0$ clearly leads to fewer errors (missed occasional summer snowfall events of very shallow depth) than falsely accounting for (far more) frequent
- 520 clouds. The Noee Bianco Pian Venezia (NBPV) catchment is an exception: we do not impose $f_{SCA} = 0$ during July and <u>August</u> since it generally has snow over the glacier also during summer. Finally, we remove small inaccuracies by applying a moving-compute the average on a window of threefractional snow cover area (F_{SCA}) for each catchment by averaging all f_{SCA} <u>values available for all snow</u> images over the f_{SCA} timeseries. in the PoC, without interpolation between the time steps. After this filtering step, we compute the average f_{SCA} (i.e., F_{SCA}) for each catchment by averaging all f_{SCA} values available for
- 525 all snow images in the *PoI*, without interpolation between the time steps.

3.5 Accounting for groundwater: fraction of quaternary deposits (F_{qd}) , Winter Flow Index (*WFI*) and baseflow fraction (F_{bf})

 3.3
 Some authors have revealed the key possibility of unconsolidated sediments (e.g., talus, moraine, alluvium)

 storing groundwater in Alpine catchments (Christensen et al., 2020; Hayashi, 2020; Arnoux et al.,

 530
 2021).Fraction of Quaternary deposits, low-flow duration and the groundwater contribution to the stream

We use the same Winter Flow Index (WFI) as Arnoux et al. (2021), as indicated by Eq. 7:



	$WFI = \frac{Q_{NM7}}{Q_{mean}} $ (7)
	The stored water in these deposits can in fact sustain streamflow during the low-flow period (Hayashi, 2020; Arnoux et al.,
	2021), i.e. during long periods without direct water input, especially during winter, which can last 6 months or more in high
535	elevation catchments. Such sustained flow during long periods points towards important amounts of stored water that is well
	connected to the streamflow network and thereby remains accessible throughout the low flow period and also during glacier
	and snowpack recession due to climate change (Somers et al., 2019). It is thus natural to think that groundwater might also
	play a key role in driving F_{yw} in Alpine catchments.
	We describe in this section how to calculate three quantities that are all, directly or indirectly, linked to groundwater: fraction
540	of quaternary deposits (F_{qd}), the Winter Flow Index (<i>WFI</i>) and baseflow fraction (F_{bf}). First, we estimate the proportion of
	quaternary deposits similarly to Arnoux et al. (2021). Operatively, for the 23 Swiss catchments of our dataset, we calculate
	the portion of the catchment area occupied by quaternary deposits using the Geological Atlas of Switzerland (GeoCover
	dataset, 1:25000 scale) freely available from the Federal Office of Topography swisstopo. We use the geological sheets that
	intersect the catchments boundaries for evaluating the portion of unconsolidated sediments area (A_{qd}) covering the
545	catchments area (A). Thus, we calculate the fraction of quaternary deposits (F_{qd}) as:
	$F_{q\bar{q}} = \frac{A_{q\bar{q}}}{A}.$ (6)
	We repeated the same procedure for the DOR and SOU catchments by using the regional geological map for obtaining this
	fraction. For the DOR and SOU eatchments the vectorized Valsavaranche geological map (1:100000 scale) is provided by
	the Cartography Office of SCT Geoportal. For the NBPV and BCC catchments the .shp of unconsolidated sediments is
550	provided by Dr. Giulia Zueceo-where Q _{NMZ} is the minimum discharge over seven consecutive days during the winter period
	(from November to June) and Q_{mean} is the mean annual discharge. We calculate it for the 27 study catchments during the
	PoS. Similarly to Arnoux et al. (2021), we calculate the portion of the catchment area occupied by Quaternary deposits (A_{qd})
	(available from National or Regional geological data set) with respect to the total catchment area (A). Thus, we calculate the
	fraction of Quaternary deposits (F_{ad}) as reported by Eq. 8:
555	$F_{qd} = \frac{A_{qd}}{A}$. The spatial cover of quaternary deposits for the 27 study catchments is reported in Fig. 1.
	To complement geological information, we also calculate the Winter Flow Index (WFI), a low-flow indicator that is
	generally used to evaluate the potential of catchments to store groundwater (Paznekas and Hayashi, 2016; Cochand et al.,
	2019; Hayashi, 2020; Arnoux et al., 2021):
	$WFI:=\frac{q_{NM=}}{q_{m}},\tag{7}$
560	where $O_{\rm NM2}$ is the minimum discharge over seven consecutive days during the winter period (from November to June) and
	φ_{mean} is the mean annual discharge (Arnoux et al., 2021).

Finally, we estimate the baseflow contribution to streamflow that is generally assimilated to the flow from groundwater and, accordingly, is associated to groundwater processes (Hall, 1968; Duncan, 2019). Additionally, Duncan (2019) provides a

specific technique that allows estimation of separate components with physical relevance in the case that baseflow separation

565

(8)

The area covered by such deposits for a sample area of our study region is reported in Fig. 6.

techniques were not applied to describe physical processes. We apply the,



570 Figure 6 Proportion of quaternary deposits (black colour) covering the area of seven study catchments in Switzerland.

To relate WFI to low flow, we apply the recent baseflow separation technique described by Duncan (2019) to the discharge time series of the 27 study catchments. Specifically, we apply it to the available discharge measurements within the temporal windows of streamwater isotope sampling. For the 22 Swiss catchments from von Freyberg et al. (2018), we consider the sampling period reported in Table 1 of their published paper. For VdN, NBPV and BCC catchments we consider the time windows November 2015 – December 2018, May 2013 – September 2015, March 2010 – October 2017, respectively. Finally, for the DOR and SOU catchments, we consider discharge measurements in the period November 2017 – January 2022. To express the groundwater contribution to streamflow in a form that is directly comparable with the young water fraction, we define the baseflow fraction (*F_{by}*) as: (within the PoS indicated in Table 1). In short, this method comprises a single backward pass through the data to fit an exponential master baseflow recession curve (Eq. 9.1), followed by a single forward pass (Eq. 9.2, Eq. 9.3) of the Lyne and Hollick (1979) algorithm to smooth the connection between segments of the master recession, simulating a gradual groundwater recharge during the runoff event (Duncan, 2019):

 $M(t_{i-1}) = \frac{M(t_i) - c}{k} + c_{-1}$

(9.1)

	$Q_q(t_i) = kQ_q(t_{i-1}) + \left(M(t_i) - M(t_{i-1})\right)^{\frac{1+k}{2}} $ (9.2)
585	$Q_{bf}(t_i) = M(t_i) - Q_q(t_i)$, (9.3)
	where $M(t_i)$, $Q_g(t_i)$ and $Q_{bj}(t_j)$ are the master recession value, the quick recession flow and the baseflow at time t_i , respectively.
	In this study, we consider daily time steps (i.e., $t_i - t_{i-1} = 1$ day). This method has 2 parameters: k is the recession constant; c is
	a constant flow added to the exponential decay component. We set the recession constant $k = 0.925$ (Nathan and McMahon,
	1990); we add no constant flow to the exponential decay (i.e., in terms of Duncan (2019) method, c=0). A Matlab © code
590	with the implementation of the Duncan (2019) baseflow filter has been made available in the Supplementary Material.
	To express the catchment storage contribution to streamflow in a form that is directly comparable to the young water
	fraction, we define the baseflow fraction (F_{bf}) as reported in Eq. 10:
	$F_{bf} = \frac{1}{n} \sum_{t=-1}^{n} \frac{Q_{tf \neq t(t_{t})}}{Q(t_{t})},$
	$\frac{(8)\sum_{i=1}^{n} \frac{Q_{bf}(t_i)}{\sigma(t_i)}}{(10)},$
595	where $Q_{bf}(t_i)$ is the baseflow (mm d ⁻¹) at the time t_i (obtained as indicated by Eq. 9.3) and $Q(t_i)$ is the discharge (mm d ⁻¹) at the time t_i . Following the 0.9 to 0.95 range recommendation for <i>k</i> of Nathan and McMahon (1990), we test the uncertainty of this value by drawing random samples (10000 values) from a normal distribution with mean 0.925 and standard deviation
	25% of the range given by Nathan and McMahon (1990) (i.e. standard deviation of 0.0125 which ensures that the 10% and
	90% sample percentiles correspond to the original range). Thereby we obtain 10000 values of F_{bf} for each catchment, of
600	which we compute the standard deviation.
	As introduced in Section 1, F^*_{yyy} can be low if the snapshot young water fraction $F_{yyy}(t_i)$ is very low for many time steps.
	Past studies revealed that $F^*_{\mu\nu}$ increases with the catchment wetness (von Freyberg et al., 2018; Wilusz et al., 2017). If we
	consider the discharge (O) as a proxy for the catchment wetness, we can reliably assert that $F(t_i)$ is low for low $O(t_i)$. Thus,
	another important variable is the duration of the low-flow period. In this study, we define a low-flow period (T_{Low}) as
605	follows:
	$T_{Low} = \forall t_i : \frac{Q_{bf}(t_i)}{Q(t_i)} \ge 0.85 \ . \tag{11}$
	Thus, a low-flow period is defined here as a period when 85% of the total flow is composed of baseflow (i.e., baseflow-

dominated). Accordingly, we define the low-flow duration (LFD), as the proportion of the time-steps (e.g., days) in the PoS that can be considered as a low flow period according to Eq. (11).

610 <u>4 Results and Discussion – Towards a harmonious and exhaustive framework of the hydrological</u> processes that drive the young water fraction variations with elevation.

We present and discuss hereafter (Section 4.1, 4.2, 4.3 and 4.4) the identified relations between F^*_{yw} and the studied explanatory variables (F_{qd} , F_{bf} , LFD and F_{SCd}), followed by the emerging perceptual model that describes the main processes driving the F^*_{yw} variations with mean catchment elevation and harmonizes our results with previous studies (Section 4.5).

615 4.1 The role of Quaternary deposits

Confirming the results of Arnoux et al. (2021), we find a negative statistically significant correlation between F^*_{yw} and WFI ($\rho_{\text{Spearman}} = -0.4$, p-value = 0.04, see Fig. S5), suggesting (unsurprisingly) that more groundwater contribution to streamflow increases the water age. WFI and F_{qd} values for all the study catchments are reported in Table 2. To analyze the relationship of F^*_{yw} with Quaternary deposits we rule out the SOU and BCC catchments since they show $F_{qd} = 0$ (see Table 2). Including

- 620 catchments with $F_{qd} = 0$ would bias the analysis since something that is absent cannot have a role in modulating the share of groundwater and thus the young water fraction in the stream. Focusing first only on the snow-dominated catchments, a linear fit on the data returns a negative slope of -0.31 ($R^2 = 0.4$), indicating a reduction of F_{yw} with increasing F_{ad} (Fig. 7a). Moreover, we find a Spearman rank correlation coefficient of -
- 0.62 with a p-value of 0.12, meaning a negative, but not statistically significant correlation between F*_{yw} and F_{qd}. This result
 can be explained by considering several factors. First, water storage in Quaternary deposits is not the only groundwater storage contribution to the stream in such environments: additional storage is provided by the bedrock fractures (Gleeson et al., 2014; Jasechko et al., 2016; Martin et al., 2021), possibly caused by rock stress and high erosion rates and by the bedrock geology, which has influence on groundwater retention capacity (Hayashi, 2020). Second, the area covered by Quaternary deposits could be a not sufficient good proxy of the groundwater storage potential: the knowledge of the thickness of these
- 630 deposits (i.e., their volume) and the bedrock topography are crucial factors for controlling groundwater storage (Arnoux et al., 2021; Hayashi, 2020) but corresponding data is not available to date.
 F*_{yw} values of the hybrid catchments reveal a weak positive correlation with Quaternary deposits (ρ_{Spearman} = 0.1, p-value = 0.81) while, for rainfall-dominated catchments, they show a negative correlation (ρ_{Spearman} =-0.5, p-value = 0.22); however,
- both correlations are not statistically significant. These weak correlations suggest that F_{qd} represents only a limited part of the catchment geology responsible for groundwater flow and that it can only be considered as a first-order measure of geological groundwater storage.

We furthermore observe that F_{qd} decreases with mean catchment elevation in our data set (Fig. 7b), revealing a negative statistically significant correlation ($\rho_{\text{Spearman}} = -0.5$, p-value < 0.01). This negative correlation reflects the fact that F_{qd} decreases when the mean slope increases (Arnoux et al., 2021).

640 <u>To conclude, we stress that more catchments and more geological information would be required to statistically validate</u> these observations about the role of the groundwater storage potential for explaining young water fraction variations.



Figure 7 a) Young water fraction against fraction of Quaternary deposits b) Fraction of quaternary deposits against mean catchments elevation

4.2 Stored (old) water contribution to streamflow (F_{bf}) and F_{yw}^*

The baseflow time series resulting from the baseflow separation of Duncan (2019) for six representative study catchments (two of each regime) are reported in Fig. 8 (complete results in Fig. S2). This figure shows the effect of groundwater 650 recharge from rain and snowmelt through the "smoothed" baseflow proposed by Duncan (2019). This "smoothing" simulates a delayed storage contribution to the stream following the recharge phase during an input event. This recharge phase promotes the system wetness, thus favoring an increasing quick flow. The increasing quick flow during events also leads to an increase of Fyw(ti), as found by previous works (von Freyberg et al., 2018). However, the relative amount of baseflow remains high during events: the average baseflow fraction during the high-flow period is 0.49 and 0.52 for hybrid and 655 rainfall-dominated catchments, while it is 0.63 for snow-dominated catchments. In agreement with worldwide stable-isotopebased hydrograph separations results (Jasechko, 2019), this outcome underlines the mobilization of stored water (i.e., old water) during rainfall and snowmelt events, and this process seems to be particularly relevant in high-elevation catchments. Accordingly, in snow-dominated systems, the snowmelt largely transits through the groundwater store (Hayashi, 2020; Cochand et al., 2019; Du et al., 2019; Flerchinger et al., 1992; Martinec, 1975), as schematized in Fig. 4, and the very high 660 baseflow in high mountain catchments during summer is a direct sign of meltwater infiltration and percolation to

groundwater that pushes old snowmelt (the main groundwater storage component) out to the stream network, as also found by Martinec (1975). This is also supported by the fact that groundwater, in such catchments, often has the isotopic signature of snowmelt (Michelon et al., 2022; Pavlovskii et al., 2018).

Looking at the overall flow (and not only at the high-flow periods), F_{bf} is generally lower for hybrid catchments (average F_{bf} = 0.67) than for rainfall-dominated (average F_{bf} = 0.74) and snow-dominated catchments (average F_{bf} = 0.83). In the BCC catchment, we find a F_{bf} (0.87) that is consistent with previous findings of Penna et al. (2016) using stable water isotopes: they have shown that, on average, from 80% to 98% of BCC discharge is composed of pre-event water (assumed to represent groundwater). The values of F_{bf} for all the study sites are reported in Table 2. On average, the F_{bf} computed over the entire PoS are higher than those computed during the high-flow periods. This result suggests, unsurprisingly, that the largest amount of stored water is released during low-flow periods. Accordingly, the variations of F_{bf} with elevation among different catchments (Fig. 9b) can be explained considering the changes in low-flow duration (LFD) with elevation, as will be discussed in Section 4.3.

Baseflow filters were already applied in previous studies and their results were correlated with F*_{yw}. For example, von Freyberg et al. (2018) found a strong positive correlation (ρ_{Spearman} = 0.73, p-value < 0.001) between F*_{yw} and the Quick-flow
Index (QFI), calculated as the average ratio between (Q-Q_{bf}) and Q, where Q is the daily discharge and Q_{bf} is the daily baseflow calculated in their paper with the Lyne and Hollick (1979) baseflow filter. Relating the F_{bf} to F*_{yw}, we have found a strong negative correlation (ρ_{Spearman} = -0.75, p-value < 0.001), showed in Fig. 9a, consistent with previous results of von Freyberg et al. (2018).

In snow-free systems, F^*_{yw} is by definition related to F_{bf} . Baseflow is composed of groundwater and groundwater is the dominant source of old water in such systems (in absence of large lakes). In snow-influenced systems, through the "direct input" approach for estimating F^*_{yw} , we consider the snowpack (i.e., a temporarily old water storage) as part of the catchment storage. However, the share of snowmelt (with age > 3 months) that flows off quickly as surface or fast subsurface runoff will not show up in F_{bf} . In other words, F_{bf} is not able to take into account all the snowmelt, but only the part of meltwater that infiltrates and recharges the groundwater storage, which is a large portion of the overall snowmelt.

685 <u>4.2.1 The complementarity between the fraction of baseflow (F_{bf}) and the young water fraction (F_{yw})</u>

A by-product of this work is that the estimated F_{bfs} applying the Duncan (2019) baseflow filter, is roughly the complementary term of F^*_{yyw} (Fig. 9a, Fig.9b) which is an important result for catchments where isotope measurements are missing. In such catchments, F^*_{yyw} could potentially be estimated without the application of the amplitude ratio approach as:

 $F_{yw}^* \simeq 1 - F_{bf},$

(12)

690 Some of our case studies show considerable "residuals" of 1- (F_{bf} + F*_{yw}) (Fig. 9b). This is partially due to the uncertainty of the parameters used for estimating F_{bf}. In this regard, Duncan (2019) suggests some calibration guidelines to obtain an optimal parameters set for baseflow estimation per catchment. In this work, we did not use the calibration guidelines, but we simply used the recession parameter proposed by Nathan and McMahon (1990) in order to achieve factual and reproducible results. In addition, the estimation of baseflow during an event is generally less rigorous than during the recession phase (Duncan, 2019), affecting the F_{bf} estimation. Moreover, F*_{yw} values are influenced by the sampling rate: the higher is the

frequency of sampling, the higher is the young water fraction (Gallart et al., 2020a; Stockinger et al., 2016). Thus, the young water fraction calculated with the "amplitude ratio" approach generally underestimates the "real" young water fraction, and we simply compensate by computing the flow-weighted young water fraction (F^*_{yu}) . In hybrid and snow-dominated catchments these "residuals" can also be explained considering that the F_{bf} does not include surface runoff or fast lateral subsurface flow of meltwater, likely older than 2-3 months, following a snowmelt event. On the other hand, these residuals might also be related to the non-linear recession behavior of catchments, which was shown by Santos et al. (2018) to be dominant for Swiss low elevation (i.e., rain-dominated) catchments, in which case the exponential recession assumption of the baseflow filter necessarily leads to less reliable results (Duncan, 2019).

700



705 Figure 8: Baseflow separation for six representative study catchments using the Duncan (2019) filter. The black area represents the daily discharge, while the coloured area represents the estimated daily baseflow where Q_{bf} is the amount of daily baseflow (mm d⁻¹) we obtain using the baseflow separation technique described in the work of Duncan (2019), Q is the daily discharge (mm d⁻¹), t_i is the time step for which we have discharge measurements (where the subscript "i" refers to a specific day) and n is the total number of days within the considered time window.

710 4 Results

4.1 Young water fraction estimation for DOR and SOU catchments

We apply the methodology described in Section 3.2 to estimate the young water fraction in DOR and SOU catchments. The unweighted F_{yw} values are equal to 0.1 \pm 0.02 for both DOR and SOU catchments. In contrast, the flow-weighted F_{yw} are 0.16 \pm 0.03 and 0.01 \pm 0.02 for DOR and SOU catchments, respectively. Thus, we find a 60% increase of the flow weighted

715 F_{yw} for the main catchment, while flow-weighted F_{yw} remains unchanged for the very small lateral subcatchment. The F_{yw} results for these two high-elevation catchments agree with F_{yw} estimated by Jasechko et al. (2016), Lutz et al. (2018), Ceperley et al. (2020), who found less young streamflow in mountains than in other landscapes.

4.2 The new hydro-climatic regime classification

Two selected variables, Q_{June}/Q_{DJF}- and F_{SC4}, classify catchments into three classes using our streamlined methodology:
 rainfall-dominated, hybrid and snow-dominated; these have the same names as the ones proposed by Staudinger et al. (2017) but the classification is not based on the same criteria.

In order to achieve a classification as consistent as possible with that of Staudinger et al. (2017), but based on these two variables, we propose the thresholds presented in Table 2:

 Table 2. New formal classification scheme for defining the catchments hydro-climatic regime using two-variables: the FSCA and

 725
 QLume/QDJF-ratio.

Condition 1	logical	Condition 2	Hydro-climatic regime
$Q_{June}/Q_{DJF} \leq 1$	æ	<i>F_{SC4}</i> < 0.3	Rainfall-dominated
$Q_{June}/Q_{DJF} \leq 1$	æ	$0.3 \le F_{SC4} \le 0.5$	Hybrid
$Q_{June}/Q_{DJF} > 1$	æ	$F_{SC4} \ge 0.5$	Snow-dominated

The catchment's hydro-climatic regimes defined with these thresholds for the two variables or classifiers are generally consistent with those of Staudinger et al. (2017) (Table S1). The only exceptions are the BIB and GUE catchments whose regimes switch from rainfall-dominated to hybrid (BIB) and vice-versa (GUE). The hydro-climatic regime switch arises for

- 730 these two catchments because their Q_{hume}/Q_{DAF} ratio are < 1, while their F_{SC4} (0.32 for BIB and 0.29 for GUE) are very close to our selected threshold of 0.3. Following our classification scheme, the 27 study catchments are equally distributed over the three classes: 8 rainfall-dominated catchments, 10 hybrid catchments and 9 snow-dominated catchments. The regime of cach catchment is reported in Table S1.
- The two selected classifiers are positively correlated ($\rho_{Spearman} = 0.89 p$ -value < 0.01). Moreover, fitting an exponential model 735 ($a - e^{bF_{SCI}}$) on the Q_{Jume}/Q_{DJE} vs F_{SCA} points, we obtain a = 0.03 (confidence bounds: $0.02 \div 0.04$) and b = 8.32 (confidence bounds: $7.95 \div 8.70$) with a very high $R^2 = 0.99$ (Fig. 3, the 95% confidence bounds of the coefficients are obtained through a robust fit using the bisquare weighting function in Matlab R2019b). This result suggests that the easy-to-calculate

Q_{Jume}/Q_{DJF} ratio is a good predictor of the snow regime, here represented by F_{SC4}. Thus, if F_{SC4} data are missing, it is possible to use the exponential relationship (Fig. 3) for a first order estimate of the second classifier. Some catchments, specifically
 SCH, ILF and EMM fall away from the curve. They are hybrid or snow-dominated catchments with large areas (> 100 km²) and wide elevation ranges (> 1400 m). In such cases the summer flow is more influenced by summer rainfall at lower elevations and snowmelt preferentially occurs during spring, reducing the Q_{Jum}/Q_{DJF} ratio. For catchments with these characteristics, the use of the exponential relationship underestimates the F_{SC4}.



745 Figure 3. Scatterplot of the 2-selected classifiers: QJune/QDJF and FSCA- It shows the strong correlation between the two classifiers.

4.3 New explanatory variables for the Fyw elevation gradients

Initial evidence of low F_{yw} in high-elevation catchments is given in the work of Jasechko et al. (2016). Based on the analysis of 254 worldwide-watersheds, their work reveals a reduction of F_{yw} in steeper terrains. A first physical explanation of this result could be related to deep vertical infiltration caused by fractures generated by the high stress that rocks have to endure in complex terrain morphologies such as those of high-elevation environments (Gleeson et al., 2014; Jasechko et al., 2016). Moreover, the higher the topographic roughness is, the longer are the flow paths, with a consequent rise of transit time (Gleeson and Manning, 2008; Frisbee et al., 2011; Jasechko et al., 2016).

Our dataset is characterized by a general increase of slope with elevation (Fig. 4a). Despite this, we do not find significant correlation between F_{yw} and mean slope (ρ_{Spearman} = -0.25, p-value = 0.22) (Fig. 4b). The correlation becomes significant only when the rainfall-dominated catchments are removed from the analysis (ρ_{Spearman} = -0.7 p-value < 0.01). This result suggests that there is an increasing rate of infiltration when the hydro-climatic regime transitions from hybrid to snow-dominated. We probed deeper into the role of snow and groundwater in lowering the F_{yw} to understand the hydrological function of these focus catchments.







water fraction against mean elevation. Bars with black edge indicate F_{bf} (left axis), while bars with grev edge indicate F^*_{pp} (right axis). Vertical bars represent +/- standard deviation.

4.3 Low-flow duration (LFD) and F^*_{yw}

- 775 The values of LFD for all the study sites are reported in Table 2. Specifically, LFD is lower for hybrid catchments (median LFD = 0.39), and it is increasingly higher for rainfall (median LFD = 0.50) and snow-dominated catchments (median LFD = 0.62). In hybrid catchments, the presence of rain and snowmelt events during large parts of the year and the relatively low (compared to rainfall-dominated catchments) evapotranspiration due to reduced temperatures (Goulden et al., 2012), strongly reduces the duration of low-flow periods, and this is also visible from the recurring discharge peaks (Fig. 8.) In low-lying,
- 780 rain-dominated catchments, evapotranspiration and precipitation are respectively higher and lower than in hybrid catchments, leading to longer low-flow periods (usually during summer and autumn). Under current climate and according to our data set, in snow-dominated catchments we observe longer winter low-flow periods (streamflow decreasing below 0.5 to 1 mm/d for the highest locations, see Fig. S6) on an annual scale than in hybrid catchments. To gain additional insights into the high LFD in snow-dominated catchments and the low LFD in hybrid catchments, it is necessary to further consider the
- 785 role of snowpack persistence, discussed in the following Section. The variations of LFD with elevation are shown in Fig. 11b.

It is well known that low-flow periods are typically baseflow-dominated (or old water dominated). Accordingly, as anticipated in Section 4.2, the variation of F_{bf} between catchments reflects the proportion of the low-flow duration during the PoS. We observe that the higher the LFD is, the higher is the F_{bf} in fact, they are strongly positively correlated ($\rho_{\text{Spearman}} =$

790 <u>0.97</u>, p-value < 0.001) as shown in Fig. 10. The negative correlation between LFD and F^*_{yw} is lower ($\rho_{\text{Spearman}} = -0.75$, p-value < 0.001, Fig. 11a) but nevertheless suggests that LFD is an important predictor for F^*_{yw} .



Figure 11 (a) F^*_{vv} against the Low Flow Duration, LFD. Boxplots of F^*_{vv} for catchments belonging to the same regime are plotted in correspondence to the median LFD. b) LFD against mean elevation.

4.4 The role of snowpack persistence

800 We next explore the presence of an ephemeral or seasonal snowpack as a relevant factor for the time-concentration of liquid water input and for LFD. We consider the F_{SCA} calculated as reported in Section 3.2, as a proxy of the snowpack persistence. The F_{SCA} values for all the study sites are reported in Table 2. The underlying f_{SCA} timeseries for six representative study





Figure 5. Timeseries of f_{SCA} for 6 representative study <u>S3</u>). All the catchments (two for each hydro-climatic regime), illustrating the gradual increase of the F_{SCA}-passing from rainfall-dominated to snow-dominated catchments.

As stated above, we calculate the F_{SCA} as a proxy of the snow-regime. High F_{SCA} values (> 0.5) correspond to catchments with characterized by a seasonal snow-cover (i.e., eatchments where the snowmelt events are concentrated during late spring and summersnow-dominated) reveal a high F_{SCA} (> 0.40, median $F_{SCA} = 0.51$). Gradually smaller F_{SCA} values refereorrespond to increasingly more ephemeral snowpacks; with intermittent snowmelt events during the winter season (Petersky and Harpold, 2018), as reflected by the spiky f_{SCA} timeseries of hybrid and rainfall-dominated catchments (Fig. 5):12).

Our results show a bell-shaped behavior of F*_{yw} with varying F_{SC4} (Fig. 13a). Specifically, we observe a general increase of F*_{yw} for F_{SC4} values roughly below 0.3. This result can be explained considering that especially in hybrid catchments
(median F_{SC4} = 0.28), but partially also in rain-dominated catchments (median F_{SC4} = 0.13), streamflow receives relatively more young water from ephemeral snowpacks. These short-lived snowpacks melt during the winter season resulting in little delay between precipitation input and melt (i.e., no water aging in the snowpack), and corresponding meltwater potentially flows off quickly into the stream (reducing LFD, Fig.14), e.g., in presence of a frozen surface soil layer. In fact, ephemeral and slightly thick snowpacks do not protect the underlying soil from freezing (Harrison et al., 2021; Rey et al., 2021). Even for low elevation locations (< ≈ 1500 m a.s.l.), freezing conditions are regularly observed during winter (Keller et al., 2017). For F_{SC4} values roughly higher than 0.3, we observe a decrease of F*_{yw} with F_{SC4}; here all the catchments of our data set are

40

snow-dominated. The mechanisms at play here are: i) in catchments with seasonal snowpacks, streamflow receives

snowmelt in spring and summer that is at least partly older than 2-3 months (because part of the snow fell more than 3 months before the melt occurs). ii) The building up of a persistent, deep snowpack can promote deep vertical infiltration

- 825 during the main melt period, either by insulating the soil and thereby preventing/reducing freezing (Harrison et al., 2021; <u>Rey et al., 2021; Jasechko et al., 2016) or by gradual soil thawing during the melt period (Rey et al., 2021; Scherler et al., 2010). The temporal dynamic of snow accumulation and melt supports the pivotal role of snowmelt in recharging groundwater during summer in high-elevation environments (Cochand et al., 2019; Du et al., 2019; Flerchinger et al., 1992). A similar result was also found for dolomitic catchments (such as BCC and OVA) by Lucianetti et al. (2020), who revealed</u>
- 830 different proportions of rain and snow contributions to the recharge of springs in the Dolomites, with a gradually higher meltwater contribution in springs with increasing elevation. This role of snowmelt supports our analytical choice of computing F*_{yw} through the "direct input" approach, thus considering the snowpack as part of the catchment storage. In addition, the potentially large shares of meltwater that recharge groundwater via deep vertical infiltration also result in old water sustaining winter baseflow (Fig. S4): the persistent snowpack and the absence of a *liquid* water input favor a groundwater storage emptying resulting in a longer winter low-flow period that increases LFD (Fig.14), thus reducing F*_{yys}
- as discussed in Section 4.3. F_{SC4} is strongly correlated with the mean catchment elevation in our data set ($\rho_{Spearman} = 0.97$, p-value < 0.01, Fig. 13b). A posteriori, we could have considered mean elevation instead of F_{SC4} as a proxy for snowpack persistence. However, a priori,
- it could be approximative to describe the snow cover persistence only with the increasing elevation: the persistence of snow
 in a catchment also depends on catchment aspect, topography (Painter et al., 2023) snow-related and climatic characteristics. In fact, catchments with very different characteristics (e.g., different elevation ranges, different areas etc.) can reveal a similar mean elevation, but the snowpack persistence could considerably change. This is the reason why we decided to focus on *F_{SC4}* that integrates these physical factors.
- The above mechanisms are not able to explain the hydrological functioning of the glacier-dominated NBPV catchment, which shows a very high F*_{yw} and is categorized as an outlier among the snow-dominated catchments (Fig. 13a). The high F*_{yw} of the high elevation glacier-covered (42%) catchment can be explained considering that the glacier-melt produces high amounts of streamflow that transit the glacier-system very quickly during the summer, given generally fast englacial and subglacial flow paths and the often limited water storage capacity in the glacier forefield (Müller et al., 2022; Saberi et al., 2019; Jansson et al., 2003). Schmieder et al. (2019) also found a high young water fraction in an Austrian glacier-covered
- 850 (35%) catchment leading them to the conclusion that the basin behaves like a 'Teflon basin' with fast transmitted ice melt, also if this behavior is differentiated in space.



0` 0

0.1 0.2 0.3

0.4 F_{SCA} (-)

Figure 13 a) Young water fraction against F_{SC4} . The grey area represents the perceptual bell-shaped behaviour of F^*_{pp} with increasing F_{SC4} b) F_{SC4} against mean elevation.

0 L 0

0.7

0.8

0.6

0.5

500

1000

1500 2000 2500 Mean elevation (m a.s.l.) 3000 3500 4000



860 Figure 14 Low-flow duration (LFD) against F_{SCA}

Table 2 F*yr, Fqd, LFD, Fbf, FSCA and WFI values for all the study catchments

ID (Regime)	<u>F*_{vw} (-)</u>	<u>Fqd (-)</u>	<u>LFD (d/d)</u>	<u>F_{bf} (-)</u>	<u>Fsca (-)</u>	<u>WFI (-)</u>
AAB (R)	<u>0.22</u>	<u>0.41</u>	<u>0.44</u>	<u>0.71</u>	<u>0.14</u>	<u>0.14</u>
AAC (R)	<u>0.10</u>	<u>0.99</u>	<u>0.50</u>	<u>0.73</u>	<u>0.11</u>	<u>0.15</u>
<u>ALL (S)</u>	<u>0.12</u>	<u>0.64</u>	0.62	<u>0.84</u>	0.45	<u>0.24</u>
<u>ALP (H)</u>	<u>0.39</u>	<u>0.61</u>	<u>0.41</u>	<u>0.69</u>	0.28	<u>0.06</u>
BCC (S)	<u>0.10</u>	<u>0</u>	<u>0.71</u>	<u>0.87</u>	<u>0.42</u>	<u>0.23</u>
<u>BIB (R)</u>	<u>0.41</u>	<u>0.61</u>	<u>0.39</u>	0.65	0.23	<u>0.06</u>
<u>DIS (S)</u>	<u>0.11</u>	<u>0.56</u>	<u>0.74</u>	<u>0.89</u>	0.58	<u>0.19</u>
DOR (S)	<u>0.16</u>	<u>0.24</u>	0.65	0.85	0.61	<u>0.06</u>
<u>EMM (H)</u>	0.35	0.53	<u>0.3</u>	<u>0.6</u>	0.28	<u>0.01</u>
ERG (R)	0.14	0.50	0.51	0.75	0.07	0.05
<u>ERL (H)</u>	0.54	<u>0.74</u>	0.21	0.50	<u>0.30</u>	<u>0.01</u>

<u>GUE (H)</u>	<u>0.19</u>	<u>0.8</u>	0.44	<u>0.71</u>	0.23	<u>0.07</u>
<u>ILF (H)</u>	<u>0.13</u>	<u>0.69</u>	0.53	<u>0.77</u>	0.22	<u>0.12</u>
LAN (R)	<u>0.07</u>	<u>0.98</u>	0.69	<u>0.87</u>	<u>0.10</u>	<u>0.40</u>
<u>LUM (H)</u>	0.37	<u>0.90</u>	0.37	0.66	0.33	<u>0.08</u>
<u>MEN (R)</u>	0.27	<u>0.93</u>	<u>0.59</u>	<u>0.79</u>	<u>0.09</u>	<u>0.18</u>
MUR (R)	<u>0.13</u>	0.62	0.53	<u>0.77</u>	0.14	<u>0.19</u>
NBPV (S)	0.33	0.24	0.35	0.7	0.76	0.00
<u>OVA (S)</u>	0.15	<u>0.41</u>	0.66	0.85	0.54	<u>0.21</u>
RIA (S)	0.21	<u>0.43</u>	0.63	<u>0.84</u>	<u>0.47</u>	<u>0.11</u>
<u>RIE (R)</u>	<u>0.2</u>	<u>0.21</u>	0.43	<u>0.68</u>	<u>0.18</u>	<u>0.07</u>
<u>SCH (S)</u>	0.15	0.62	0.61	0.85	<u>0.47</u>	0.20
<u>SEN (H)</u>	<u>0.30</u>	<u>0.5</u>	0.49	0.75	0.22	0.24
<u>SIT (H)</u>	<u>0.19</u>	<u>0.54</u>	0.35	<u>0.68</u>	<u>0.28</u>	<u>0.07</u>
<u>SOU (S)</u>	<u>0.10</u>	<u>0</u>	0.56	0.82	0.53	0.01
<u>VdN (S)</u>	0.08	0.49	0.62	0.84	0.49	0.04
VOG (H)	0.34	0.48	0.39	0.66	0.27	0.07

The identified key drivers of young water fractions for rainfall-dominated, hybrid and snow-dominated catchments can conveniently be summarized into a perceptual model of the involved hydrological processes and their seasonal interplay

4.5 Process interplay along elevation: perceptual model

<u>(Fig. 15).</u>

High-elevation catchments are characterised by long winter low-flow periods, resulting from the build-up of a seasonal
snowpack, and sustained by the emptying of groundwater (or old water) storage. Accordingly, such storage releases stored water, mainly old meltwater, for prolonged periods where the snowpack can last for several months (typically from December to early April) before releasing water during the melting season. Such seasonal snowpack can protect the underlying soils from freezing, favouring meltwater infiltration and groundwater recharge. From this viewpoint, snowpack is considered as part of the catchment storage and there is a thin line between groundwater and meltwater in snow-dominated

880 catchments. Snowmelt or rain events push out old meltwater to the stream during summer, as suggested by the relatively high amount of daily baseflow during the melting season. During this period, the high catchment wetness might even lead to saturation and thereby favour fast flow paths of meltwater or rainwater, which in turn can temporarily increase the young



water fraction. Despite this increase during high-flow periods, the prevailing winter low-flow periods in such systems lead to a reduction of the average annual young water fraction.

- 885 In catchments with an ephemeral snowpack, at lower elevations, snowmelt events occur regularly during winter such that water released from the corresponding short-lived snowpack is likely younger than 3 months. Moreover, ephemeral snowpacks do not protect the underlying soils from freezing and rapid flow paths can emerge during episodic or long-term soil surface freezing, increasing the young water fraction. The high F^{*}_{yw} of such systems is also explained by the simultaneity of snowmelt and rain events during extended parts of the year (leading to large volume of annual precipitation)
- 890 and the relatively low (compared to rainfall-dominated catchments) evapotranspiration. Both processes increase the catchments wetness and reduce the low-flow periods length. Finally, at the lowest elevations, lower amounts of precipitation and higher evapotranspiration favour longer low-flow

periods, mainly sustained by old groundwater from alluvial aquifers, which lead to both a F^*_{yw} and catchment wetness reduction. Further, the relatively flat topographies at the lowest elevations favour slow flow paths increasing the transit times of water.

How well current hydrological models can represent the interplay of these processes along elevation gradients is left for future research, but our perceptual model builds a solid basis for an improvement of theory-driven models (Clark et al., 2016).





Figure 15 Perceptual model of the hydrological processes that drive the young water fraction variations with elevation. This model emerges from our analysis and harmonizes these results with those of previous studies. For snow-dominated and hybrid catchments, we indicate the dominant processes, occurring during summer and during winter, that lead to low and high F^*_{max} respectively.

905 <u>5 Conclusion</u>

This study proposes a conceptualization of the processes behind changes in young water fraction (F^*_{yv}) with elevation, defined here following Kirchner (2016a) as water that is younger than 2-3 months. The analysis is based on young water fractions for a set of 27 study catchments located in Switzerland and Italy which span a wide range of geological and hydroclimatic conditions. Our analysis focuses on mountainous catchments to fill the knowledge gap referring to the surprisingly low young water fractions at high elevations (> 1500 m a.s.l.), but we have also considered catchments at lower elevations to

- 910 low young water fractions at high elevations (> 1500 m a.s.l.), but we have also considered catchments at lower elevations to obtain a complete picture of the dominant hydrological processes at different elevations.
 We have focused on variables and processes that were not previously considered for explaining elevation gradients of young water fraction. We have investigated the role of i) the groundwater storage potential ii) the catchment storage contribution to
- 915 the stream iii) the low-fow duration iv) the snowpack persistence. Our results suggest that ii) iii) and iv) are connected to 916 each other: low-flow periods are generally sustained by old water deriving from the catchment storage and the length of such 917 periods is driven by the snowpack persistence at high elevations. The proportion of low-flow periods during the period of 918 isotope sampling strongly influences the amount of old water contributing to the stream, thus reducing the estimated F*_{vvv}.

Consequently, the low-flow duration, which varies with elevation, can be retained as driver of the F*yw changes with elevation. Given the importance of low-flow periods, we have also investigated the role of groundwater storage potential,
 represented here by the portion of catchment area covered by Quaternary deposits. Our results suggest that this analysis should be completed with more detailed geological information e.g., the geology and topography of bedrock, the fraction of

- should be completed with more detailed geological information e.g., the geology and topography of bedrock, the fraction of fractured bedrock and the deposits' thickness, which is challenging to retrieve from geological data set. We have finally harmonized the results of this analysis in a perceptual model that describes a framework for how hydrological processes control the F^*_{uv} according to elevation, laying the foundations for an improvement of theory-driven models.
- 925 The strong complementarity between $F^*_{,yw}$ and the average fraction of baseflow obtained for our data set suggests that $F^*_{,yw}$ could be estimated starting from automated baseflow separation techniques for catchments in which stable water isotopes measurements are not available. This complementarity should however be validated in future work, considering e.g., alternative baseflow separation techniques and different hydro-climatic conditions.
- Finally, the conceptualization of the hydrological processes described in this paper do not fit the high young water fraction of
 the single glacier-dominated catchment of our data set. In conclusion, we encourage future studies to compare and to collect isotopic data from glacier-dominated catchments to better understand the processes in such systems that, under glacier retreat due to climate change, will see a gradual transition to purely snow-dominated systems.

 Data availability. Time series of both δ²H and δ¹⁸O in streamflow and precipitation for the 22 Swiss catchments investigated

 935
 by
 von
 Freyberg
 et
 al.
 (2018)
 are
 available
 in
 the
 data
 repository
 Zenodo
 at

 935
 by
 von
 Freyberg
 et
 al.
 (2018)
 are
 available
 in
 the
 data
 repository
 Zenodo
 at

 https://zenodo.org/record/4057967#.Y00oMHZBxPY
 (Staudinger
 et al.,
 2020).
 Meteorological,
 hydrological
 and
 isotope

 data
 of
 VdN,
 BCC
 and
 NBPV
 catchments
 are
 available
 at:

 https://onlinelibrary.wiley.com/action/downloadSupplement?doi=10.1002%2Fhyp.13937&file=hyp13937-sup-0009 Supinfo2.zip. For the existing data set, we used the values of F^*_{3W} (direct-input) reported in Fig. 4c of von Freyberg et al.

- 940 (2018), kindly provided by the corresponding author, and in Table 6 of Ceperley et al. (2020) with associated errors. Daily discharge data for the ERL, LÜM and VOG catchments are provided by the *Swiss Federal Institute for Forest, Snow and Landscape research (WSL)*, Birmensdorf, Switzerland. Streamflow data for the AAB and GUE catchments are provided by the *Office for Waste, Water, Energy and Air (WWEA)* of the Canton of Zurich and by the *Office for Water and Waste* of the Canton of Bern, respectively. Daily discharge data of the remaining 17 Swiss catchments studied by von Freyberg et al.
 945 (2018) are provided by the *Swiss Federal Office for the Environment (FOEN)*.
- The .shp of the AAB, GUE, ERL, LÜM and VOG catchments boundaries are available from the data repository Zenodo at https://zenodo.org/record/4057967#.Y000MHZBxPY (Staudinger et al., 2020). The .shp of NBPV, BCC and VdN catchments, are provided by Dr. Giulia Zuecco and Dr. Anthony Michelon (University of Lausanne, Switzerland) as personal communication. The DOR and SOU catchments boundaries are delineated in a GIS environment using the 10-m resolution.
- 950 Digital Elevation Model (DEM) available from the Aosta Valley Regional Geoportal. Finally, the catchment boundaries of

the remaining 17 Swiss catchments investigated by von Freyberg et al. (2018) are directly obtained from the Swiss Federal Office for the Environment (FOEN).

<u>Quaternary cover for all Swiss catchments has been calculated using the Geological Atlas of Switzerland (GeoCover data</u> set, 1:25000 scale) available from the *Federal Office of Topography swisstopo*. For the DOR and SOU catchments the

- 955 vectorized Valsavaranche geological map (1:100000 scale) is provided by the *Cartography Office of SCT Geoportal*. For the NBPV and BCC catchments the .shp of unconsolidated sediments is provided by Dr. Giulia Zuecco, Our results highlight a different median *F_{yw}* for each hydro-elimatic regime (Fig. 6), with similar low values for rainfall-dominated catchments (median *F_{yw}* of 0.16) and snow-dominated catchments (median *F_{yw}* of 0.14) but much higher values for hybrid catchments (median *F_{yw}* of 0.32), which in addition shows higher dispersion (Fig. 6). We observe a general increase of *F_{yw}* as long as the
- 960 F_{SC4} remains below roughly one third or more exactly 0.38 (median f_{SC4} for hybrid catchments) and a subsequent lowering of F_{yw}-when F_{SC4} is higher than this threshold. In fact, considering only catchments with a F_{SC4} ~ ~ 0.38, we obtain a statistically significant positive correlation between F_{yw} and F_{SC4} (p_{Spearman} = 0.72, p-value < 0.01). In contrast, catchments with a F_{SC4} > ~ 0.38, aside from NBPV, show a negative statistically significant correlation (p_{Spearman} = -0.5, p-value < 0.1). We exclude the NBPV glacier-dominated catchment since its F_{SC4} and F_{yw} relationship is an outlier compared to the other snow-dominated catchments. Note that ERL and ALP catchments are included in both correlations since their F_{SC4} is very close to 0.38. Thus, it is difficult to reliably allocate these catchments to either the "rising" or "falling" limbs of the F_{yw}-F_{SC4}.



Figure 6. F_{yw} against F_{SCA}. The vertical bars are as in Fig. 4b. The boxplots show the median, quartiles, and whiskers (extending to 970 the most extreme data points not considered outliers, the latter indicated with the '+' red symbol) of the F_{yw}-values per-regime type, centered on the corresponding median f_{SCA}-value per regime type (0.20, 0.38 and 0.56).

4.3.2 The role of quaternary deposits

To advance our understanding of the process that drives F_{yw} according to elevation gradient, we analyze the correlation between the fraction of unconsolidated deposits (F_{ad}) and the young water fraction (Fig. 7), assuming that groundwater is

975 stored in unconsolidated sediments. We exclude the SOU and BCC catchments from our analysis, which show F_{qd} = 0.
 Considering only the 9 snow dominated catchments, i.e., the group having the features as close as possible to those used by Arnoux et al. (2021), we find a Spearman rank correlation coefficient of -0.5 with a p-value of 0.22, meaning a negative, but not statistically significant correlation between F_{yw} and F_{qd}. F_{yw} values of the 10 hybrid catchments reveal a positive, but non-significant correlation with unconsolidated sediments (p_{Spearman} = 0.4, p-value = 0.29). Finally, rainfall-dominated catchments
 980 show a negative, non-significant correlation (p_{Spearman} = 0.52, p-value = 0.2).



-Figure 7. Plot of Fyw against the fraction of quaternary deposits (Fqd)

4.3.3 Groundwater contribution to streamflow: WFI and F_{bf} related with F_{yw}

Analysis by Arnoux et al. (2021) revealed that the fraction of quaternary deposits is positively correlated with the low-flow
 indicators (e.g., WFI) in high-elevation catchments. This evidence indicates that catchments with high WFI receive an important contribution from groundwater (Arnoux et al., 2021). This is also confirmed by our dataset (Fig. 8a). Indeed, if we look at snow-dominated catchments, always removing the SOU catchment since it shows a F_{qd} = 0, we find a positive and statistically significant correlation (pspearman=0.67 p-value < 0.1) of F_{qd} with the WFI. Conversely, we do not find statistically significant correlations for hybrid (negative correlation) and rainfall-dominated (positive correlation) catchments. In
 exchange, WFI is negatively and significantly correlated with the young water fractions of the entire dataset (pspearman=-0.40)

p-value < 0.1) as shown in Fig. 8b.



Figure 8. a) Fraction of quaternary deposits plotted against WFI; b) Young water fraction plotted against WFI.

As described in Section 3.5, we apply the baseflow filter of Duncan et al. (2019) to the daily discharge data of the 27 study catchments for having a more physical evaluation of the groundwater contribution to streamflow. The resulting baseflow time series are reported in Fig. 9 for the selected six representative study catchments (time series for all the study sites are available in the Supplementary Material, Fig. S3).

To directly compare the F_{yw} with the amount of baseflow, considered here as a proxy for groundwater, we calculate the average fraction of baseflow (F_{by}) as reported in Section 3.5. We obtain a strongly negative and significant correlation of F_{yw} with F_{by} (p_{Spearman}= -0.75 p-value < 0.01) as shown in Fig. 10. The F_{by} is generally lower for hybrid catchments (median F_{by} of 0.67) than for rainfall-dominated catchments (median F_{by} of 0.74) and snow-dominated catchments (median F_{by} of 0.84).

- Moreover, the fit of a line of F_{yw} as a function of F_{bf} points (*cftool*, Matlab R2019b) demonstrates a complementary relationship ($\mathbb{R}^2 = 0.65$): $F_{yw} = -(0.93 \pm 0.19)F_{af} + (0.91 \pm 0.22)$, (9)
- 1005 Interestingly, we find that the NBPV catchment has a lower F_{bf} (≈ 0.7) if compared to the median F_{bf} of catchments belonging to the same regime. All the results in terms of median values per regime are summarized in Table 3. The full results table (Table S1) for all catchments is available in the Supplementary Material.





1010 Figure 9.-Baseflow separation for six representative study catchments using the Duncan (2019) filter. The black area represents the daily discharge, while the coloured area represents the estimated daily baseflow.







	rainfall-dominated		hybrid		snow-dominated	
	median IQR		median	IQR	median	IQR
F.,(-)	0.16	0.10	0.32	0.16	0.14	0.09
F_{bf} (-)	0.74	0.07	0.67	0.10	0.84	0.02
WFI (-)	0.15	0.11	0.07	0.06	0.11	0.17
F_{qd} (-)	0.71	0.50	0.57	0.19	0.43	0.3 4
F_{SCA} (-)	0.20	0.11	0.38	0.09	0.56	0.11
Q_{June}/Q_{DJF} (-)	0.26	0.10	0.47	0.41	3.74	2.95

1020 Table 3. Summary table with all the results in terms of median values with associated Inter Quartile Range (IQR) for each hydroclimatic regime.

5 Discussion

5.1 The new hydro-climatic regime classification

025 For each of the three hydro-climatic regimes, it is possible to define an average characteristic shape of the monthly hydrograph (Fig. 11). A shift of the monthly hydrograph peak of about 1.5 months is observed passing from rainfalldominated (peak in March) to hybrid catchments (peak in mid-April) and then, passing from a hybrid to a snow-dominated (peak in June) regime (Fig. 11). This "flow peak-shifting" is a clear sign of the increasing predominance of snowmelt in the streamflow generation processes and is at the basis of Pardé Coefficient based regime classifications. Accordingly, the value

030 of the elassification proposed here is not to shed new light on streamflow dynamics but to objectively connect the streamflow regime shape to summer-to-winter streamflow ratios and to the mean snow cover extent. The new classification scheme can be applied outside Switzerland and the objective and explicative classifiers, on which it is based, allow the study of regime changes (e.g., from snow-dominated to hybrid) that will become increasingly more apparent under climate change (Lucianetti et al., 2020; Harrison et al., 2021).



Figure 11. Coloured areas represent the monthly flow of each study catchment. The solid lines indicate the average monthly flow for each hydro-climatic regime, thus defining a characteristic shape of the monthly hydrograph for each of such regimes. Dashed black lines show the month in which, on average, the peak-flow is observed for each hydro-climatic regime.

5.2 A perceptual model: snowpack persistency favours increasing water age.

040 A perceptual model that describes the theoretical behavior of young water fraction with varying F_{SCA} emerges from our analysis and harmonizes the results of this work with that of previous studies.

A plot of F_{SC4} against F_{yw} (Fig. 12a) shows a bell-shaped behavior (which we visualize with the grey shade in Fig. 12a) that suggests the interplay of two different trends: a positive trend as long as $F_{SC4} \simeq 0.38$ and a negative trend for $F_{SC4} \simeq 0.38$. This threshold (that is the median f_{SC4} of hybrid catchments) splits the hybrid regime in two sub-classes.

- 045 The first sub-class (elevation <≈1500 m a.s.l.) is mainly influenced by the rain-dominated regime. Accordingly, the rising limb of the bell shaped curve can be primarily explained by the increase of precipitation and slope with elevation (Fig. 12a, Fig. 4a) and the reduction of evaporation with elevation due to reduced temperatures (Goulden et al., 2012). As elevation increases, these factors favor an ever-growing lateral and longitudinal connectivity (Tromp-van Meerveld and McDonnell, 2006; McDonnell, 2013; McDonnell et al., 2021) producing wetness conditions that promote rapid flow paths: the young</p>
- 1050 water fraction increases but also groundwater recharge; this promotion of groundwater recharge is visible in a plot of winter baseflow against elevation (Fig. S4). In addition, higher order channels, higher up, are more rarely activated than lower order channels that are more often active (Botter et al., 2021; Durighetto et al., 2022). Therefore, it is more likely that lower order channels are draining more old water than the temporary activated higher order channels: water age decreases with elevation when catchments reveal a negligible or a shallow, possibly ephemeral, snowpack. In fact, the limited number of snowfall
- 1055 days and mid-winter melt reduce the snow accumulation in the lower elevation sub-class of hybrid regimes. Such a snowpack does not protect the underlying soils from freezing (Harrison et al., 2021). Even for low elevation locations (< ≈1500 m asl.), freezing conditions are regularly observed during winter (Keller et al., 2017): such conditions can lead to soil

freezing thereby inhibiting infiltration and favoring rapid flow paths during mid-winter melt events, with subsequent increase $\alpha f E_{rec}$

- 1060 In contrast, the second sub-class (elevation > ≈1500 m a.s.l.) of hybrid catchments is increasingly influenced by the snow-regime. Here, the building up of a persistent, deep snowpack can promote deep vertical infiltration by insulating the soil and thereby preventing freezing (Jasechko et al., 2016; Harrison et al., 2021). The resulting effect on water partitioning between the surface and the subsurface has however to be analyzed in light of the temporal concentration of water input on the snowmelt period and remains largely unexplored to date (Rey et al., 2021). Despite of this, the temporal dynamic of snow accumulation and melt and its effect on deep infiltration supports the pivotal role of snowmelt in recharging groundwater
- during summer in high-elevation environments (Flerchinger et al., 1992; Cochand et al., 2019; Du et al., 2019). Moreover, the analysis of Lucianetti et al. (2020) revealed different varying proportions of rain and snow contributions to the recharge of springs in the Dolomites according to elevations. Specifically, they observed a gradually higher snowmelt contribution in springs passing from roughly 46% below 2000 m a.s.l to nearly 72% above 2500 m a.s.l. To advance our understanding of
- 1070 F_{yw} along elevation gradients, we also need to ask how and when groundwater storage contributes to streamflow. Here, another crucial function of the seasonal snowpack comes into play: it favors the emptying of the groundwater storage over long winter recession periods. In some snow-dominated environments, the seasonal snow cover can persist for more than six months, and the streams correspondingly show a low flow regime resulting from absence of rain and melt-input, with minimum flow during winter decreasing below 0.5 to 1 mm/d for the highest locations (Fig. S5). It is assumed that these
- 1075 low-flow periods, generally consistent from year to year because of the annual temperature cycle, are sustained by the groundwater storage that provides resilience to Alpine rivers (Hayashi, 2020). This groundwater (or old water) contribution to streamflow during the winter period increases the age of streamwater. In addition, high elevation catchments can reveal winter low-flow periods that are significantly longer than their high flow periods (Hayashi, 2020). In conclusion, this low-flow period strongly influence the water age, thereby decreasing the *F*_{yw}-
- 1080 The above mechanisms are summarized in the perceptual model reported in Fig. 13 also indicating which are the dominant processes over the winter and summer seasons. This model is, however, not able to explain the NBPV catchment hydrological functioning, which is classified as snow-dominated according to our classification criterion, but our criterion does not consider the influence of glaciers. The NBPV catchment area is 42% glacier covered, so it is probable that this catchment should belong to a fourth class of "glacier dominated" catchments (in fact, it is detected as an outlier: see blue
- boxplot in Fig. 12a). Such catchments could show fast flow paths and small storages as e.g. discussed in the work of Jansson et al. (2003), reviewing glacier dominated environments. Moreover, reduced baseflow during winter can be related to increasingly high temperatures causing the glaciers retreat, thus reducing and anticipating the glacier melt fluxes that possibly recharge groundwater (Hayashi, 2020).



090 Figure 12. a) Theoretical behavior of young water fraction with varying FSCA indicated by the grey area b) Fyw as function of mean catchment elevation. The dashed red line indicates the threshold elevation above which the Fyw-reset is observed.

5.3 The role of unconsolidated sediments in increasing or decreasing water age

- 095 We have achieved correlation that is not statistically significant between F_{qd} and F_{yw} that can be explained considering that unconsolidated sediments are not the only groundwater storage contribution to the stream during low flow periods in such environments. In steeper catchments, additional storage is provided by the bedrock fractures (Gleeson et al., 2014; Jasechko et al., 2016; Martin et al., 2021) and by the bedrock geology which has influence on groundwater retention capacity (Hayashi, 2020). However, necessary data is elusive.
- 100 The positive-correlation between F_{yw} and F_{qd} in hybrid catchments-can be explained by two mechanisms: i) high-baseflow points towards system saturation being high, which favors connectivity and ii) ephemeral snowpacks can favor freezing phenomena inhibiting winter snowmelt infiltration and thereby favoring fast flow processes (Harrison et al., 2021). Concluding, we stress that more catchments and more geological information would be required to statistically validate these observations.

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Figure 13. Perceptual model of different hydrological functioning of catchments characterized by ephemeral snowpacks, in panels 110 b (winter) and d (summer), and by seasonal snowpacks, panels a (winter) and c (summer).

5.4 Groundwater contribution to streamflow is the key to understand F_w gradients

We have tested here if the counterintuitive low F_{yw} obtained for high-elevation catchments depends on the groundwater contribution to streamflow and if the results are consistent with our perceptual model. We obtain a statistically significant negative correlation between F_{yw} and F_{bb} (Fig. 10) and the linear fit of the points suggests that F_{bb} is roughly the one's

complement of F_{yw} . This result clearly indicates that the observed patterns of F_{yw} are related to water partitioning between the surface and the subsurface. Moreover, this complementarity gives a further physical meaning for the estimated baseflow in our data set: the estimated baseflow should correspond to water with transit times higher than roughly 0.2 years.

We find the highest F_{bf} for snow-dominated catchments confirming the presence of high subsurface storage, contributing to 120 streams, in high-elevation catchments (Staudinger et al., 2017). Moreover, the annual baseflow is strongly positively correlated with the F_{SC4} (ρ_{Spearman} = 0.81 p-value < 0.01) suggesting a major groundwater contribution with increasing snow cover persistency (Fig. S6).

The major dispersion of F_{bf} we find in hybrid catchments supports the idea that such catchments can reveal a different hydrological functioning depending on whether they are mainly influenced by the rain or snow regime. The hydro-climatic regime is generally a good indicator of the proportion of young water that contributes to streamflow, with a few exceptions

though. Interestingly, the F_{bf} offers an explanation for these exceptions. For example, the BCC catchment is classified as hybrid, but it reveals a low F_{yw} (0.11) that is comparable with those obtained for snow-dominated catchments (median F_{yw} = 0.14). In fact, BCC reveals a F_{SC4} of 0.45, very close to the threshold of 0.5 for being classified as snow-dominated (Table 2) and a high F_{bf} (0.87) underlining the dominant role of groundwater in the streamflow generation. This result is consistent with previous findings of Penna et al. (2016) for this catchment: they have shown that, on average, from 80% to 98% of

BCC discharge is constituted by pre-event water (assumed to represent groundwater).

Another special case is the NBPV catchment: it is an outlier in the F_{yw} - F_{SC4} -space (Fig. 12a, i.e., the perceptual model is not able to explain its high F_{yw}) but it results to be in line with the other catchments in the F_{yw} - F_{bf} -space (Fig. 10) and its relatively high F_{yw} -(0.34) can reasonably be explained with a relatively low F_{bf} -(0.70, i.e. a relatively low groundwater 135 contribution to streamflow).

Therefore, we can conclude that the contribution of groundwater storage to streamflow, which is driven by snowpack duration, can be considered as the best explanatory variable of the $F_{\gamma w}$ elevation gradients.

6<u>1</u>Conclusion

This paper demonstrates, based on a new collection of observations of high-elevation catchments from both published
datasets and new field observations, that Alpine young water fractions, F_{pwr} show a topographic pattern that is characterized with an increase to about 1500 m a.s.l., and a decrease thereafter. We provide here an explanation for this pattern, thereby elarifying why F_{pwr} is low in high-elevation catchments, filling a knowledge gap expressed in previous studies. All the study catchments have been classified in three categories: rainfall-dominated, hybrid or snow-dominated. We do this through a new classification scheme that can be applied using objective and parsimonious classifiers: the summer/winter discharge
ratio (Q_{Jume}/Q_{DJF}) and the fractional snow cover area (F_{SCA}). These classifiers strongly correlate; therefore, it is possible to use the easy to calculate Q_{Jume}/Q_{DJF} for obtaining a first-order estimate of F_{SCA} through the exponential relationship proposed in this paper.

We focus on the correlations between F_{yw} and three selected variables: the fraction of quaternary deposits, F_{qd}, F_{SC4}, and the fraction of baseflow, F_b, Additionally, we consider the Winter Flow Index (WFI) for comparing our results about the 150 groundwater contribution to streamflow with those of previous works.

- The fraction of quaternary deposits (F_{qd}), assumed to store groundwater, does not produce a statistically significant eorrelation with F_{yw} ; however, this analysis should be completed with more detailed geological information, e.g., the bedrock geology or the fraction of fractured bedrock, which is hard to retrieve in geological data set.
- The relationship between F_{yw} and F_{SC4} shows a bell-shaped curve that suggests the activation of different hydrological processes depending on the snowpack duration (ranging from ephemeral to seasonal). Building from this observation, we develop a perceptual model of how snow persistency explains F_{yw} -during winter and summer along topographic gradients: during winter, at elevations with an ephemeral snowpack (< 1500 m a.s.l.), high system wetness and soil freezing favor rapid flow paths leading to high F_{yw} ; at elevations with a seasonal snowpack (> 1500 m a.s.l.), there is almost no water input during winter and streamflow is fed by progressively emptying groundwater storage, leading to low F_{yw} . These seasonal snowpacks insulate soils, thereby promoting deep vertical infiltration on the snowmelt onset and supporting the
- pivotal role of snowmelt in recharging groundwater storage in high mountain environments during summer. This recharge leads to high baseflow throughout the year, especially during winter, and only few streamflow events characterized by fast flow paths. Since winter low flow periods can be longer than high flow periods in snow-dominated catchments, such periods influence the water age at annual scale and thereby lead to decreasing *F*_{yw} with winter duration (i.e., with elevation).
- 165 This perceptual model is corroborated by the high negative correlation between F_{bb} and F_{yw}, which indicates a key-role of groundwater in streamflow generation processes and further confirmed by the negative and significant correlation between WFI and F_{yw}. Nevertheless, our model is not able to explain the hydrological functioning of the single glacier-dominated catchment in our dataset, even if we can explain its high F_{yw} by the relatively low groundwater contribution (i.e., low F_{bb}). Thus, further research is necessary to conceptualize the processes of such systems that under glacier retreat will see a gradual transition to purely snow-dominated systems.

Data availability.

DOR and SOU data are available from Alessio Gentile upon reasonable request. Data of the remaining 25 eatchments are freely available online and all the data sources are eited in the manuscript

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<u>Code availability</u>. A GEE script for calculating Snow Cover Area and Cloud Cover Area time series over a region of interest has been made available at: https://code.earthengine.google.com/8239cfe7aab498180e5c42475023cb80?noload=true. A Matlab © code with the implementation of the Duncan (2019) baseflow filter is available with the Supplementary Material of this article.

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Supplement. The supplement related to this article is available online at

Author contributions. AG, NC, BS and SF identified the research gap, defined the methodology, developed the perceptual model₃ and prepared the paper. AG analyzed the data set. DG, DC, MP and SF collected the water samples for the DOR and 1185 SOU catchments. GZ analyzed spatial data related to NBPV and BCC catchments. All authors revised the manuscript and gave final approval to the submitted version.

Competing interests. The authors declare that they have no conflict of interest.

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