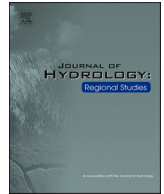




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# The signal of snowmelt in streamflow and stable water isotopes in a high mountain catchment in Central Spain

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## ABSTRACT

*Study region:* Peñalara catchment, in the mountains of the Central System in Spain,

*Study focus:* For the first time, we investigated the streamflow and streamwater isotopes during the snow accumulation and melting periods and over subsequent months in two snow seasons. The aim is to better understand the hydrological processes linked to snowmelt; to describe the temporal evolution and the interannual differences in isotopic streamwater; and to improve the understanding about the hydrological functioning of snowmelt water across the catchment.

*New hydrological insights for the region:* The isotopic signal of the streamwater progressively became isotopically depleted from the beginning of the melt period until the snow cover depletion of the catchment. Higher snowfall led to depleted isotopic values in the stream compared to a year with low snowfall. The interannual variability of the isotopic signature of streamwater during snowmelt may represent a difficulty to establishing reference values to be used in mixing models for hydrograph separation. The streamflow isotopic values had very limited sub-daily variation and showed slow temporal changes, suggesting a central role for alpine aquifers in explaining the hydrological functioning of the catchment, pointing to piston flow as a key process in streamflow generation.

## 1. Introduction

Most mountain headwaters exhibit high runoff relative to precipitation, and are essential in providing water to lowland areas (Biemans et al., 2019; López-Moreno et al., 2011; Viviroli et al., 2007). In mountain areas, snow has a major influence on the shape of the annual hydrograph by storing the precipitation that falls during the cold period in the snowpack which later melts in late spring or early summer (Morán-Tejeda et al., 2014). Snow is especially important under the climatic conditions that occur in Mediterranean

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mountains, where most of the annual precipitation falls in winter, followed by a long, dry and warm period. In these locations, the storage of snow helps to meet the high demand for water by ecosystems, agriculture, and tourism activities during the warm and dry season (Fayad et al., 2017; López-Moreno et al., 2017).

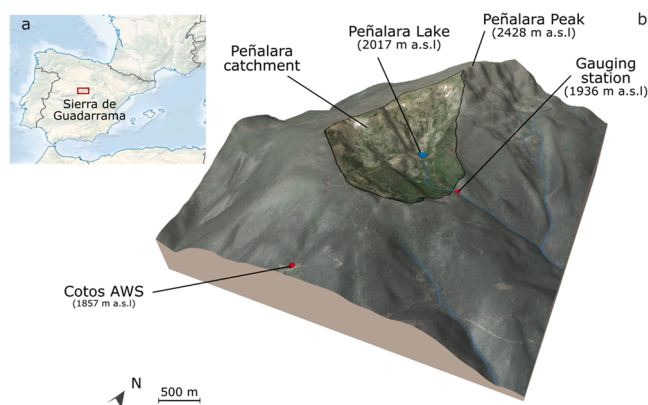
Given the importance of snow to the environment and its socioeconomic relevance in large areas of the world (Gilaberte-Búrdalo et al., 2014; Sturm et al., 2017; Winkler et al., 2018), interest has grown in quantifying the contribution of snowmelt to total runoff, and assessing the sensitivity of snow hydrology to global warming (Blöschl et al., 2019; López-Moreno et al., 2020; Musselman et al., 2021; Simpkins, 2018). For this purpose, stable water isotopes have been used as natural tracers to differentiate snowpack melt water from other runoff sources (i.e. liquid precipitation or groundwater) (Holko et al., 2018). These tracers have also been useful in inferring water flow paths and travel times through drainage areas (Ala-aho et al., 2017; Birkel and Soulsby, 2015; Jung et al., 2020). However, disentangling the various contributions to the hydrograph is difficult because of the complexity in the timing and phase shifts of the input signals (precipitation and snowmelt), combined with the inherent complexity of the landscape and storage systems (Holko et al., 2018).

In this study, we focused our research on a high mountain stream in the Peñalara Massif, within the Sierra de Guadarrama National Park (Central Spain). This mountain area has a seasonal snowpack that is subject to large interannual variability in terms of thickness and duration. The hydrological role of snow in this area has not yet been assessed. The effect of snowmelt on the shape of the hydrograph is unclear, as well as the routing and transit time of precipitation and snowmelt in these mountain areas. The impermeable lithology and steep slopes, typical of the mountains of Central Spain, suggest that the hydrological response to precipitation events should be fast, with short transit times through the basin. However, the abundance of deep talus slopes and morainic deposits suggests that groundwater stored in these so-called alpine aquifers (Hayashi, 2020) could have impacts that have not been considered to date.

In view of the above mentioned unknowns, this study aims to determine how snowmelt shapes the hydrograph, and how routing and transit time of precipitation and snowmelt controls the catchment response. For this purpose, we investigated the snow dynamics and climate conditions in the catchment, the isotope composition of precipitation and streamwaters. Twice daily streamwater and daily precipitation samples were collected over two contrasting water years: 2017 which was one of the snowiest years in recent decades; and 2018 which was a very poor snow year. The samples were used to: i) evaluate how the snowpack affected runoff timing and the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  isotopes in both precipitation and streamwater during the melt period; ii) determine whether the snowpack caused changes in the isotopic composition during the two study snow years; and iii) determine the existence or absence of sub-daily fluctuations in the streamflow characteristics to infer the time that melt water and precipitation water took to reach the basin outlet.

## 2. Study area

The study area is in the Central System in the Iberian Peninsula, in the Sierra de Guadarrama National Park, 60 km north of Madrid. The studied basin (the Peñalara catchment; Fig. 1) has a surface area of 1.36 km<sup>2</sup> and a maximum elevation (the Peñalara Peak; 40°51'N, 3°57'W) of 2428 m a.s.l. The gauging station where runoff is measured and streamwater was sampled is located at 1936 m a.s.l. The nearest automatic weather station (AWS) is 2 km from the gauging station, at Puerto de Los Cotos (1857 m a.s.l.), and includes a precipitation collector (Durán et al., 2017; Palacios et al., 2003). The Peñalara cirque is composed by an orthogneiss substratum partially covered by Quaternary deposits derived from glacial and periglacial processes, such as moraines, scree slopes, and hollows (Palacios et al., 2003; López-Olmedo et al., 2020). These materials act, in conjunction with the network of fractures and diclases, as aquifers or shallow water reservoirs in which water circulation does not usually reach more than 10 m deep. Discharge from these deposits results in surges and springs on the slopes of the Peñalara massif, with flow rates of a few litres per second (Yélamos et al., 2019). The hydrochemical characteristics of the groundwater are like those of the surface water, with low conductivity, slightly acidic pH and calcium-sodium bicarbonate-chloride facies (Yélamos et al., 2019). No isotope analysis of groundwater is available. The



**Fig. 1.** A: Location of the study area, the Peñalara catchment in the Sierra de Guadarrama. B: The Peñalara catchment is shown with a black line (3D view of a Sentinel-2 image wrapped on the topography). The positions of the gauging station at the mouth of the catchment and the nearest automatic weather station are shown by red dots.

vegetation is related to elevation. Relatively dense *Pinus sylvestris* forests grow up to 1900 m a.s.l., while the upper area of the catchment is dominated by shrubs (*Cytisus oromediterraneus* and *Juniperus alpina*), and terrain above 2100 m a.s.l. is mostly covered by alpine meadows (*Festuca curvifolia*) and bare rocks (Palacios et al., 2003). Peñalara Lake (127 m long; maximum depth 4.5 m) is located within the catchment at an elevation of 2017 m a.s.l. Its drainage area encompasses approximately 30 % of the total catchment area.

The mean annual number of days having snow cover at the Cotos AWS during the period 2014–2020 was 82 days. The effect of snow on the hydrological regime of the catchment is shown in the delayed hydrological response to monthly precipitation (Fig. 2). Precipitation data reflected the occurrence of two wet periods (November–December that sums 450 mm and March–April that sums 370 mm). Despite precipitation in the fall is larger to the one in spring, the runoff peak in spring was slightly larger. Spring runoff peak also showed a temporal delay to the precipitation peak because of the melting of the snowpack. Thus, runoff in May was  $58,9 \text{ L s}^{-1}$  with only a precipitation of 91 mm. During the fall precipitation and runoff peaks were synchronous. The annual minimum precipitation and streamflow period occurred from July to September.

### 3. Methods

#### 3.1. Water sampling and isotope analysis

Streamflow water samples for isotope analysis were collected twice daily from the Peñalara Stream by officers of the Sierra de Guadarrama National Park. The samples were collected manually at the gauging station (Fig. 1) at approximately 09:00 h (generally under very low snowmelt conditions) and 17:00 h (generally close to the daily peak melt period). The samples were transported in an isothermal bag, and stored at  $+6 \text{ }^\circ\text{C}$  at the National Park office in small bottles (10 mL) with no head space, to avoid evaporation. The transport never lasted more than one hour, so evaporation was prevented. Samples of precipitation water were collected from a sheltered against radiation precipitation collector early in the morning on the day following any snowfall or rainfall. The precipitation samples (also for isotope analyses) were treated in a similar manner like the streamflow samples. When precipitation was collected as snow, it was slowly melted in the fridge to avoid fractionation. Six samples were discarded because of their suspicious deviation in D-excess. The continuous sampling period commenced on 2 April 2018, just prior to the maximum snow accumulation recorded that year, and ceased on 3 August. More samples were taken at the end of August and in early September, when the minimum streamflow occurred. Continuous sampling commenced again on 26 January 2019, following the first substantial winter snowfall, and ceased on 17 July, when the typical minimum annual runoff levels were reached. Once a year, all the water samples were transported under cold conditions to the laboratory of the Pyrenean Institute of Ecology (CSIC).

Water isotope analyses of precipitation and streamwater were performed at the Pyrenean Institute of Ecology (IPE-CSIC, Spain) using a Picarro L2130-I wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) instrument (Picarro Inc., Sunnyvale, CA, USA). For precipitation and streamwater, aliquots of water were filtered and filled in 2 mL glass vials and sealed with rubber/aluminium caps. Water was then injected using a syringe eight times directly into the vaporisation unit of the analyser and the three first values were discarded due to memory effect. Drift correction was made using raw data and analytical uncertainty of measurements was typically 0.1 ‰ for  $\delta^{18}\text{O}$  and 0.5–1 ‰ for  $\delta\text{D}$ . The robustness of the results is guaranteed by calibration with International Atomic Energy Agency (IAEA) standards analyzed before and after every 9–10 samples. Oxygen ( $\delta^{18}\text{O}$ ) and hydrogen ( $\delta\text{D}$ ) isotope ratios were given in permil (‰) using the delta notation and are reported against Vienna Standard Mean Ocean Water (VSMOW). A total of 95 precipitation (snowfall or rainfall) and 571 streamwater samples were analyzed in this study.

#### 3.2. Climate and snow data

Precipitation and snow depth data used in this study were obtained from the Cotos meteorological station (Fig. 1). Precipitation

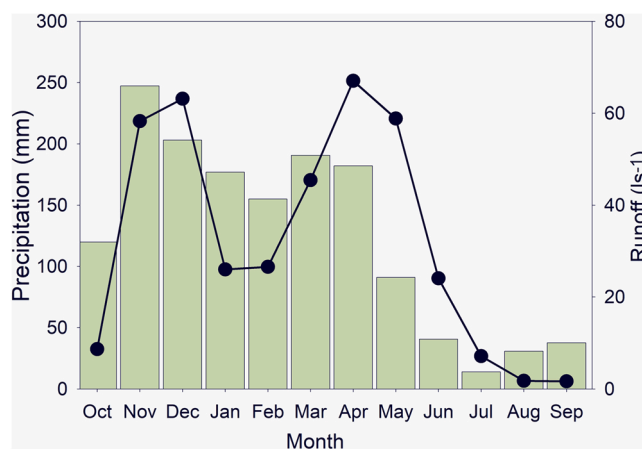


Fig. 2. Average monthly precipitation (bars) and streamflow (line) for the 2014–2020 period in the study area.

every 10 min was measured using a Geonor T200B all-weather vibrating wire load gauge. Data were converted into daily totals. Two data sources were used to characterize the snowpack, and to define the accumulation, melt, and post-melt periods. First, the depth of the snow cover was measured every 10 min using an ultrasonic range finder (Campbell SR50A; <https://www.campbellsci.es/sr50a>, last accessed on 15/08/2021) installed at the Cotos meteorological station. Second, we extracted data from the Sentinel-2 snow cover products that are available for the study area in the Theia Snow collection for the water years 2017 and 2018 (Gascoin et al., 2020). These products provide data on the absence or presence of snow cover every five days at a grid resolution of 20 m (cloud-permitting). Given the small size of the study catchment and its 5-day revisit time, Sentinel-2 was the best source of satellite data to characterize the snow cover area and temporal variability.

### 3.3. Data analysis

Based on snow cover, each snow season was separated into four periods including: (i) the accumulation period, which ran from the first appearance of snow cover until the last day that 100 % of the area was snow covered; (ii) the melt period, which followed the accumulation period until the snow cover depletion date defined by the presence of snow in less than 5 % of the basin; (iii) the first month (30 days) after the snow cover depletion date; and (iv) the second month after the snow cover depletion date. In this study, we use water years (WY, i.e. period between October 1st of one year and September 30th of the next year) instead of calendar years because part of the precipitation that falls in autumn and early winter accumulates as snow and does not drain until the following spring.

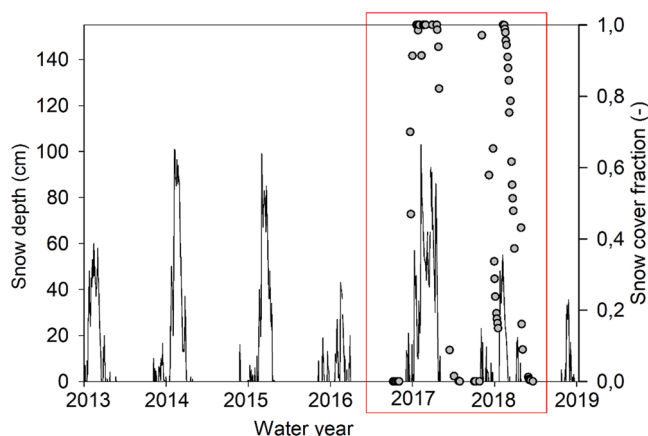
The isotope composition of precipitation water was differentiated according to the phase of the precipitation of the day: liquid (rainfall), solid (snowfall), or mixed (rainfall and snow). The phase of precipitation was recorded by the observer of the weather station.

Daily fluctuations in the isotope composition of the streamflow was calculated as the ratio of the isotope values determined for the morning and evening samples each day.

## 4. Results

### 4.1. Snow variability in the Peñalara catchment

The snow depth at the Cotos meteorological station showed marked interannual variability between 2014 and 2020 (Fig. 3). In 2015, 2016, and 2018, the snowpack was persistent and reached 1 m depth, while in other years (e.g., 2017, 2019, and 2020) the snow cover was intermittent, rarely reaching 50 cm depth and remaining present for only short periods. In relatively snow rich water years (such as WY2017, the catchment was completely covered by snow for almost three months. In WY2018, the snowpack was ephemeral until late January, with only rare snowfalls fully covering the catchment for only a few days. The snowpack disappeared at the Cotos meteorological station in late March; only isolated snowfalls occurred during April; and the catchment was completely snow-free since early June. The strong differences in water stored as snow in WY 2017 and 2018 also affected to the whole Central System as reported by the monitoring program performed by the General Directorate of Water of the Spanish Government ([https://www.miteco.gob.es/es/agua/temas/evaluacion-de-los-recursos-hidricos/vafn-ater-por-cordillera\\_tcm30-539431.png](https://www.miteco.gob.es/es/agua/temas/evaluacion-de-los-recursos-hidricos/vafn-ater-por-cordillera_tcm30-539431.png)).



**Fig. 3.** Snow evolution in the Peñalara catchment. A: Daily snow depth (lines) at the Cotos meteorological station from 2014 to 2020, and snow cover fraction (percentage of the catchment covered by snow, circles) for the Peñalara catchment from Sentinel-2 data. Red square highlights the two analyzed years in the study.

4.2. Temporal evolution of the streamflow response and stable water isotopes

The marked differences in snow cover and snow duration between the water years 2017 and 2018 (Fig. 4B) resulted in very different hydrological responses in the catchment (Fig. 4C). A long and sustained period of low levels of streamflow (only interrupted by isolated precipitation events) observed during February and March WY2017 was followed by a period of sustained high levels of streamflow during melting period (Fig. 4C). The very wet conditions, alternating solid and liquid precipitation events (547 mm of total precipitation at Cotos station during March and April), prior to the freshet suggest increased catchment storage that could also contribute to explain the very high levels of streamflow. The hydrological response of the catchment shows a progressive depletion and it was almost exhausted one month after snow cover depleted in the entire catchment. Streamflow from August to November was close to  $0 \text{ L s}^{-1}$ . The streamflow during the cold period in WY2018 generally exceeded that in the previous year, despite the lower precipitation (518 and 253 mm from January to March in WY2017 and WY2018 respectively) and spring streamflow during the melting period was markedly lower (shown also in Fig. 5), with a single peak of runoff coinciding with some rain events (that accumulated

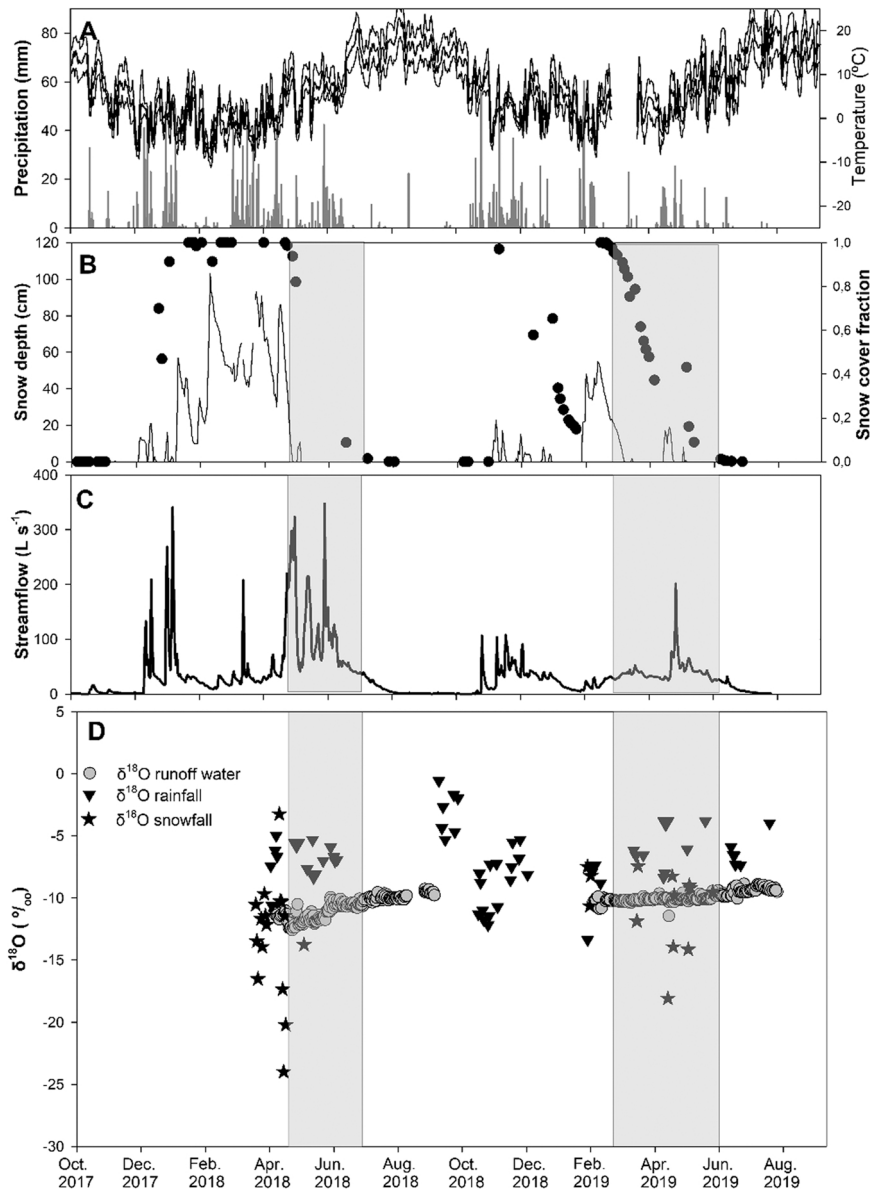
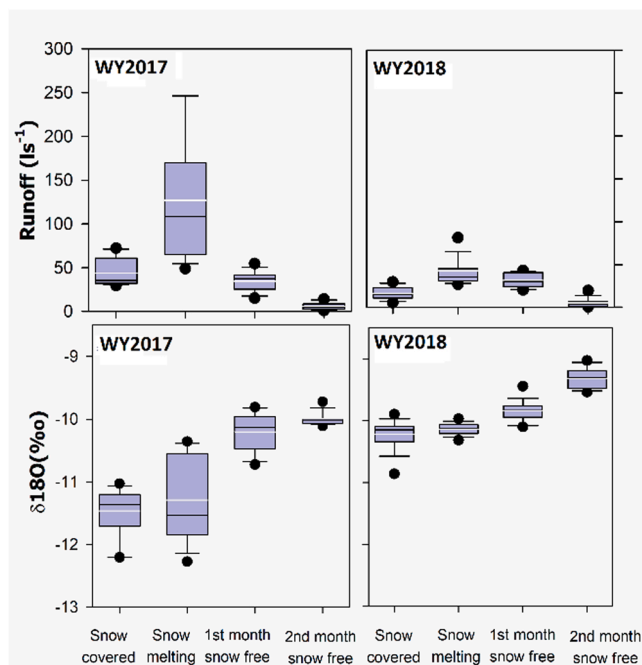


Fig. 4. A: Daily precipitation (grey bars) at the Cotos meteorological station, and daily maximum, minimum and average (thicker line) temperature. B: Daily evolution of snow depth (line) at the Cotos meteorological station and snow cover fraction (percentage of the catchment covered by snow, dots) in the catchment. C: Daily evolution of streamflow. D: Mean daily relative quantity of  $\delta^{18}\text{O}$  in runoff and precipitation (rainfall and snowfall). Dates between the shaded areas correspond to the main melt periods characterized by snow cover fraction values ranging from 1 to 0,05.



**Fig. 5.** Boxplots showing the daily variability in streamflow and streamwater  $\delta^{18}\text{O}$  during the periods when the catchment was fully covered by snow, the period of snow cover depletion (melting), and the first and second months after snow was completely depleted. The solid and dotted lines indicate the mean and the average, the boxes are the 25th and 75th percentiles, and the bars show the 10th and 90th percentiles.

160 mm) that melted the modest snowpack that had accumulated by April.

In 75 % of snowfall events,  $\delta^{18}\text{O}$  ranged from  $-13$  to  $-8$  ‰ (Fig. 4D). However, by the end of March and early April in WY2017, four snowfall days occurred on which the values ranged from  $-25$  to  $-15$  ‰. The rainfall isotope value ( $\delta^{18}\text{O}$ ) ranged from  $-10$  to  $-3$  ‰ for 80 % of the events. However, the values in a series of rainfall events in autumn WY2018 ranged from  $-15$  to  $-10$  ‰, only four events showed values higher than  $-3$  ‰ to 0 ‰.

The streamwater isotopic signal ( $\delta^{18}\text{O}$ ) showed values close to  $-13$  ‰ at the beginning of the sampling period (early April WY2017), following the very low snowfall values recorded in the preceding days. Later, the streamwater isotope values became progressively higher, with a steeper rise during the first part of the melt period (until early June), followed by a more gentle increase. The increase was even slower from the snow cover depletion date until the sampling ceased (the end of August). At that time, the streamwater isotopic signal was approximately  $-10$  ‰. The melt period in WY2018 began with markedly lower values in the streamwater ( $\delta^{18}\text{O}$  value of  $-12.2$  ‰) compared with WY2017 ( $\delta^{18}\text{O}$  value of  $-10.1$  ‰). During the entire sampling year there was a progressive change in the isotopic signal, independently of the occurrence of precipitation events or of the observed runoff peak, from  $-10.2$  in early February until values of  $-9.5$  ‰ at the end of the sampling period (early August WY2018). In both years, the isotope composition of precipitation varied markedly among rain and snow events, but no direct influence of the precipitation type on the streamwater isotopic composition was found, as the isotopic composition gradually evolved from the cold to the warm periods.

Fig. 5 summarizes the temporal evolution of streamflow and streamwater  $\delta^{18}\text{O}$  during the periods when the catchment was fully covered by snow, in the period of snow cover depletion (melting), and in the first and second months after the snow was completely depleted. This figure clearly illustrates the impact of a winter that had more precipitation and a thicker snowpack (WY2017), which generated high levels of sustained runoff during melting. On dates exceeding one month after the snow depletion date the catchment runoff was very low in both years, with values that rarely exceeded  $5 \text{ L s}^{-1}$ .  $\delta^{18}\text{O}$  values showed an inverse but synchronous pattern, with the lowest  $\delta^{18}\text{O}$  and the highest values occurring during the main accumulation and melt periods, and a marked increase in  $\delta^{18}\text{O}$  values during the first month during the snow-free period in WY2017, or later on WY2018. Differences among periods were much more marked during WY2017. The  $\delta^{18}\text{O}$  values at the end of the sampling period for WY2017 were similar to those recorded in WY2018 at the beginning of the sampling period, when the basin was completely covered by snow. An ANOVA analysis revealed that isotopic composition of streamwater was not statistically different when compared to snow covered and snow melting periods, nor when 1st and 2nd snow-free months are compared. However, there are statistically significant differences ( $p < 0.01$ ) between values for snow covered and snow melting periods, and between the values of 1st and 2nd snow-free months.

#### 4.3. Daily fluctuations of streamflow and the streamwater isotopic signal

Daily fluctuations in the streamflow (ratio between maximum and minimum daily values) were very low when the catchment was completely covered by snow and at the very end of the melt period, but the streamflow showed marked sub-daily fluctuations during

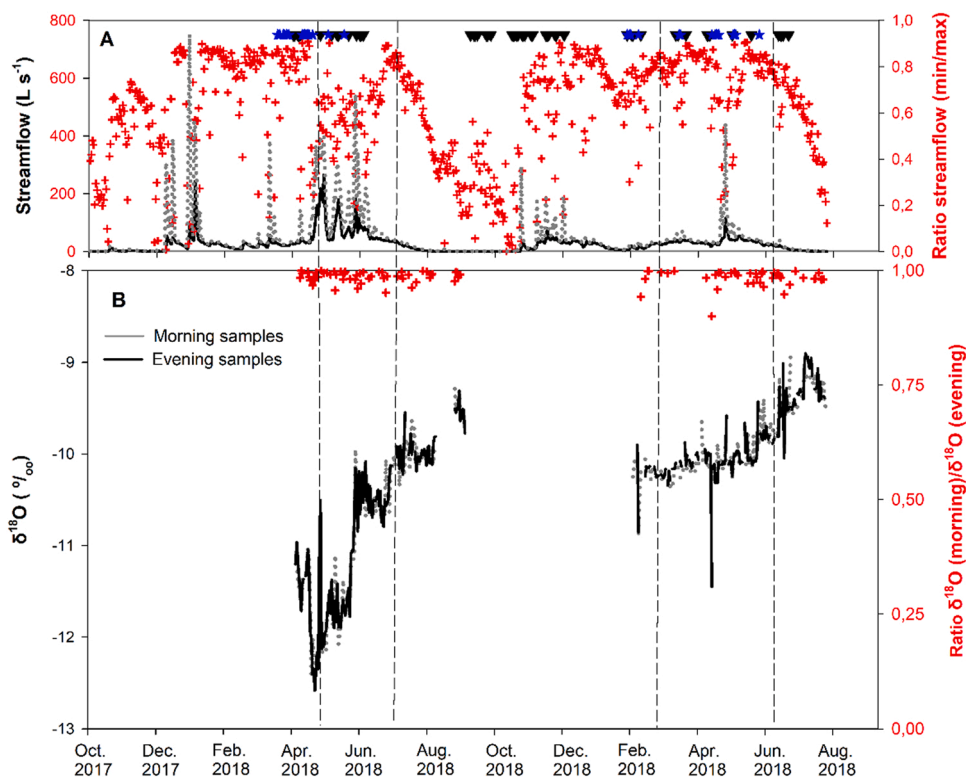


the main melt period (Fig. 6). During the months following snow depletion, the fluctuations again increased, as the streamflow declined and approached the base flow conditions. The daily fluctuations of streamflow during the warm period may have been associated with the daily cycle of evapotranspiration, similarly to what has been found in other alpine catchments (Lundquist and Cayan, 2002; Woelber et al., 2018). The daily fluctuations during the melt period were markedly more intense and sustained over time during the snow rich year (WY2017). Some other periods, in January and March 2017 and November 2018, show high daily fluctuations of streamflow out of the main melting periods. It corresponds to periods with very low streamflow values for which small variations of streamflow in absolute (e.g. liquid precipitations events) may lead to high relative variations. In contrast, the daily fluctuations of  $\delta^{18}\text{O}$  were very low, with almost no temporal pattern. The major fluctuations were observed during days when liquid precipitation occurred, but most were similar to or lower than the instrument measurement error.

## 5. Discussion

Lower and more variable isotope compositions were found during snowfall, and higher and less variable isotope values were associated with rainfall events. During both years, the streamwater isotope values showed a continuous increase from the beginning of the melt period to the end of the sampling period. This temporal evolution is very similar to that reported in other studies focused on melt waters (Dietermann and Weiler, 2013; Fan et al., 2014; Feng et al., 2002; Holko et al., 2013; Lee et al., 2010). This pattern is generally associated with a transition in the relative contributions from snowmelt to more rain and groundwater to the stream as temperature is warmer; and also with isotope fractionation during ablation, sublimation, and refreezing of the snowpack during the melt period (Dietermann and Weiler, 2013; Fan et al., 2014). Research conducted in other snow dominated sites also point out that the isotopic composition of snowfall is very variable in time and space due to the source of the atmospheric moisture and to altitudinal effects (Beria et al., 2018; Niewodnizański et al., 1981). However, the isotopic composition of the snowpack becomes more homogeneous, specially at the melting time (Holko et al., 2020, 2013; Penna et al., 2014). In this sense, the occurrence of rain on snow events can also isotopically enrich the snowpack composition.

The results strongly suggest that the different snow accumulations in the two study years led to marked differences in the streamwater isotope values, and their temporal evolution. The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values were consistently lower during WY2017 (snow abundant) than WY2018 (low snow year), and the highest values reached in the warm period of WY2018 were very close to those at the beginning of the melt period of that year. However, the differences cannot be associated only with the larger volume of melted snow during the snow abundant year; they must also be related to the very low values for solid precipitation just prior to the commencement



**Fig. 6.** A: Maximum (grey line) and minimum (black line) daily streamflows and their ratio (red crosses). Triangles (black) and stars (blue) indicate days having liquid and solid precipitation, respectively, at the Cotos meteorological station. B: The streamwater isotopic signal ( $\delta^{18}\text{O}$ ) for water samples taken in the morning (dotted grey line) and the evening (black line), and their ratio (red crosses).

of the melting period in WY2017. This finding is consistent with those of Lee et al. (2010), who found that the initial isotope composition of snowfall is important in determining the evolution of the isotope composition of the snowpack and its meltwaters, leading to marked interannual variability in the streamwater isotopic signal. Such interannual variability indicates the existing uncertainty when using stable water isotopes to determine the contribution of snowmelt to total runoff without isotope measurements of the precipitation.

The increase in  $\delta^{18}\text{O}$  over the late melt seasons and following months in each of the two study years was not strongly influenced by rainfall inputs into the snowpack, and the slope of the increase did not change significantly when snowmelt finished and the basin was free of snow. This pattern, and the very small sub-daily fluctuations in the isotopic signal during the accumulation, melt, and post-melt phases suggest a long transit time in the catchment for water inputs from snowmelt and precipitation. This is somewhat surprising, given the small size of the catchment and its impermeable granitic lithology and large areas of rocky outcrops. It is likely that Peñalara Lake, which drains 34 % of the catchment surface area and has a mean turnover time of 9 days (Toro et al., 2006), plays a role in mixing water inputs over several days, and so buffers some of the potential daily and sub-daily variability in water inputs (Leach and Laudon, 2019). However, this is not a sufficient explanation of the steady evolution of isotope enrichment and the absence of sub-daily fluctuations. The most plausible explanation is groundwater storage in coarse sediments (e.g., talus and moraines) that act as alpine aquifers (Hayashi, 2020; Tague and Grant, 2009). These types of deposits are abundant in the catchment and have an important role in the underground hydrology (Yélamos et al., 2019). The importance of the groundwater storage must explain that single isotope inputs are not quickly transferred to stream response.

Although the runoff has a relatively direct response to water inputs (showing sub-daily cycles), in particular during snowmelt period in snow dominated catchments (Krogh et al., 2022), the absence of variability in the isotope composition suggests that alpine aquifers acted as an intermediate reservoir. The Peñalara Massif has greater subsurface drainage than the surrounding mountains, where most of the streams are dry or have very low baseflow during the warmest and driest period, suggesting the importance of groundwater contributions (Yélamos et al., 2019). Thus, as has been hypothesized for river basins of Svalbard (Blaen et al., 2014), we assume that daily melt water or rainfall infiltrates into alpine aquifers and displaces the previously stored water (piston flow), rather than following a direct meltwater or rainfall runoff scheme (Yang et al., 2012). A similar process has been observed in other alpine areas dominated by snowmelt (Balestra et al., 2022; Woelber et al., 2018).

Future research should consider a more intense spatial and temporal water sampling in the catchment, including vertical gradients of precipitation, snowpack, water of the lake, groundwater and springs. This data would confirm the hypotheses developed in this study about the hydrological functioning of the catchment, and would open the possibility to perform model analyses to quantitatively discern the role of snowmelt and liquid precipitation in the hydrological response during spring and early summer.

## 6. Conclusions

The results of this study highlight the marked influence of snow on the Peñalara catchment hydrology, the high interannual variability of isotope values in streamwater, and the importance of alpine aquifers in the catchment, which is representative of many mountain areas in central Spain. The different snow conditions affected the magnitude of the spring freshet by delaying and increasing the spring peakflow during the snow abundant year, but also the H and O isotopic signals in the streamwater. The streamwater  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values showed in both analysed years increasing values from the beginning of the melt period to the warm and dry summer period. However, the values in the warm period of WY2017 were similar to those at the beginning of the melt period in the snow poor WY2018. This interannual variability highlights the difficulty in establishing reference values for streamflow coming from snowmelt. However, such reference values are often used in mixing models attempting to quantify the contribution of melt to total runoff.

The steady isotope enrichment independent of the occurrence of precipitation events or the complete depletion of snow cover in the basin, and the absence of daily fluctuations in the isotope composition of the water, suggest the involvement of alpine aquifers in storing and mixing melt water and precipitation. This stored water is displaced to the river channel through subsurface flow in direct proportion to new inputs of water entering the aquifer, explaining the occurrence of marked daily and sub-daily fluctuations in streamflow during the melt period.

## CRedit authorship contribution statement

**Juan Ignacio López Moreno:** Conceptualization, Methodology, Writing – original draft. **Ignacio Granados:** Resources, Data curation, Methodology, Writing – review & editing. **Ceballos-Barbancho:** Writing – review & editing. **Enrique Morán-Tejeda:** Formal analysis, Writing – review & editing. **Jesús Revuelto:** Data curation, Writing – review & editing. **Esteban Alonso-González:** Writing – review & editing. **Gascoin, S.:** Methodology, Writing – review & editing. **Javier Herrero:** Methodology, Writing – review & editing. **Cesar Deschamps-Berger:** Writing – review & editing. **Jerome Latron:** Conceptualization, Writing – review & editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



## Data Availability

Data will be made available on request.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.ejrh.2023.101356](https://doi.org/10.1016/j.ejrh.2023.101356).

## References

- Ala-aho, P., Tetzlaff, D., McNamara, J.P., Laudon, H., Kormos, P., Soulsby, C., 2017. Modeling the isotopic evolution of snowpack and snowmelt: testing a spatially distributed parsimonious approach. *Water Resour. Res.* 53, 5813–5830. <https://doi.org/10.1002/2017WR020650>.
- Balestra, V., Fiorucci, A., Vigna, B., 2022. Study of the trends of chemical–physical parameters in different Karst aquifers: some examples from Italian alps. *Water*. <https://doi.org/10.3390/w14030441>.
- Beria, H., Larsen, J.R., Ceperley, N.C., Michelon, A., Vennemann, T., Schaeffli, B., 2018. Understanding snow hydrological processes through the lens of stable water isotopes. *WIREs Water* 5, e1311. <https://doi.org/10.1002/wat2.1311>.
- Biemans, H., Siderius, C., Lutz, A.F., Nepal, S., Ahmad, B., Hassan, T., von Bloh, W., Wijngaard, R.R., Wester, P., Shrestha, A.B., Immerzeel, W.W., 2019. Importance of snow and glacier meltwater for agriculture on the Indo-Gangetic Plain. *Nat. Sustain.* 2, 594–601. <https://doi.org/10.1038/s41893-019-0305-3>.
- Birkel, C., Soulsby, C., 2015. Advancing tracer-aided rainfall–runoff modelling: a review of progress, problems and unrealised potential. *Hydrol. Process.* 29, 5227–5240. <https://doi.org/10.1002/hyp.10594>.
- Blaen, P.-J., Hannah, D.M., Brown, L.E., Milner, A.M., 2014. Water source dynamics of high Arctic river basins. *Hydrol. Process.* 28, 3521–3538. <https://doi.org/10.1002/hyp.9891>.
- Blöschl, G., Bierkens, M.F.P., Chambel, A., Cudennec, C., Destouni, G., Fiori, A., Kirchner, J.W., McDonnell, J.J., Savenije, H.H.G., Sivapalan, M., Stumpp, C., Toth, E., Volpi, E., Carr, G., Lupton, C., Salinas, J., Széles, B., Viglione, A., Aksoy, H., Allen, S.T., Amin, A., Andréassian, V., Arheimer, B., Aryal, S.K., Baker, V., Bardsley, E., Barendrecht, M.H., Bartosova, A., Batelaan, O., Berghuijs, W.R., Beven, K., Blume, T., Bogaard, T., Borges de Amorim, P., Böttcher, M.E., Boulet, G., Breinl, K., Brilly, M., Brocca, L., Buytaert, W., Castellari, A., Castelletti, A., Chen, X., Chen, Yangbo, Chen, Yuanfang, Chiffard, P., Claps, P., Clark, M.P., Collins, A.L., Croke, B., Dathe, A., David, P.C., de Barros, F.P.J., de Rooij, G., Di Baldassarre, G., Driscoll, J.M., Duethmann, D., Dwivedi, R., Eris, E., Farmer, W.H., Feiccabrin, J., Ferguson, G., Ferrari, E., Ferraris, S., Ferraris, B., Finger, D., Foglia, L., Fowler, K., Gartsman, B., Gascoïn, S., Gaume, E., Gelfan, A., Geris, J., Gharari, S., Gleeson, T., Glendell, M., Gonzalez Bevacqua, A., González-Dugo, M.P., Grimaldi, S., Gupta, A.B., Guse, B., Han, D., Hannah, D., Harpold, A., Haun, S., Heal, K., Helfricht, K., Herrnegger, M., Hipsey, M., Hlaváčiková, H., Hohmann, C., Holko, L., Hopkinson, C., Hrachowitz, M., Illangasekare, T.H., Inam, A., Innocente, C., Istanbuloglu, E., Jarihani, B., Kalantari, Z., Kalvans, A., Khanal, S., Khatami, S., Kiesel, J., Kirkby, M., Knoben, W., Kochanek, K., Kohnová, S., Kolechikina, A., Krause, S., Kremer, D., Kreibich, H., Kunstmann, H., Lange, H., Liberato, M.L.R., Lindquist, E., Link, T., Liu, J., Loucks, D.P., Sivapalan, C., Mahé, G., Makarieva, O., Malard, J., Mashtayeva, S., Maskey, S., Mas-Pla, J., Mavrova-Guirguinova, M., Mazzoleni, M., Mernild, S., Misstear, B.D., Montanari, A., Müller-Thomy, H., Nabizadeh, A., Nardi, F., Neale, C., Nesterova, N., Nurtaev, B., Odongo, V.O., Panda, S., Pande, S., Pang, Z., Papacharalampous, G., Perrin, C., Pfister, L., Pimentel, R., Polo, M.J., Post, D., Prieto Sierra, C., Ramos, M.-H., Renner, M., Reynolds, J.E., Ridolfi, E., Rigon, R., Riva, M., Robertson, D.E., Rosso, R., Roy, T., Sá, J.H.M., Salvadori, G., Sandells, M., Schaeffli, B., Schumann, A., Scolobig, A., Seibert, J., Servat, E., Shafiei, M., Sharma, A., Sidibe, M., Sidle, R.C., Skaugen, T., Smith, H., Spiessl, S.M., Stein, L., Steinsland, I., Strasser, U., Su, B., Szolgay, J., Tarboton, D., Tauro, S., Thirel, G., Tian, F., Tong, R., Tussupova, K., Tyralis, H., Uijlenhoet, R., van Beek, R., van der Ent, R.J., van der Ploeg, M., Van Loon, A.F., van Meerveld, I., van Nooijen, R., van Oel, P.R., Vidal, J.-P., von Freyberg, J., Vorogushyn, S., Wachniew, P., Wade, A.J., Ward, P., Westerberg, I.K., White, C., Wood, E.F., Woods, R., Xu, Z., Yilmaz, K.K., Zhang, Y., 2019. Twenty-three unsolved problems in hydrology (UPH) – a community perspective. *Hydrol. Sci. J.* 64, 1141–1158. <https://doi.org/10.1080/02626667.2019.1620507>.
- Dietermann, N., Weiler, M., 2013. Spatial distribution of stable water isotopes in alpine snow cover. *Hydrol. Earth Syst. Sci.* 17, 2657–2668. <https://doi.org/10.5194/hess-17-2657-2013>.
- Durán, L., Rodríguez-Muñoz, I., Sánchez, E., 2017. The Peñalara mountain meteorological network (1999–2014): description, preliminary results and lessons learned. *Atmosphere*. <https://doi.org/10.3390/atmos8100203>.
- Fan, Y., Yaning, C., Li, X., Li, W., Li, Q., 2014. Characteristics of water isotopes and ice-snowmelt quantification in the Tizinafu River, north Kunlun Mountains, Central Asia. *Quat. Int.* 380–381. <https://doi.org/10.1016/j.quaint.2014.05.020>.
- Fayad, A., Gascoïn, S., Faour, G., López-Moreno, J.I., Drapeau, L., Page, M.L., Escadafal, R., 2017. Snow hydrology in Mediterranean mountain regions: a review. *J. Hydrol.* 551. <https://doi.org/10.1016/j.jhydrol.2017.05.063>.
- Feng, X., Taylor, S., Renshaw, C.E., Kirchner, J.W., 2002. Isotopic evolution of snowmelt 1. A physically based one-dimensional model. *Water Resour. Res.* 38, 35–38. <https://doi.org/10.1029/2001WR000814>.
- Gascoïn, S., Barrou Dumont, Z., Deschamps-Berger, C., Marti, F., Salgues, G., López-Moreno, J.I., Revuelto, J., Michon, T., Schattan, P., Hagolle, O., 2020. Estimating fractional snow cover in open terrain from Sentinel-2 using the normalized difference snow index. *Remote Sens.* <https://doi.org/10.3390/rs12182904>.
- Gilaberte-Búrdalo, M., López-Martín, F., Pino-Otín, M.R., López-Moreno, J.I., 2014. Impacts of climate change on ski industry. *Environ. Sci. Policy* 44. <https://doi.org/10.1016/j.envsci.2014.07.003>.
- Hayashi, M., 2020. Alpine hydrogeology: the critical role of groundwater in sourcing the headwaters of the world. *Groundwater* 58, 498–510. <https://doi.org/10.1111/gwat.12965>.
- Holko, L., Danko, M., Dosa, M., Kostka, Z., Sanda, M., Pfister, L., Iffly, J.F., 2013. Spatial and temporal variability of stable water isotopes in snow related hydrological processes. *Bodenkultur* 64, 39–45.
- Holko, L., Bičárová, S., Hlavčo, J., Danko, M., Kostka, Z., 2018. Isotopic hydrograph separation in two small mountain catchments during multiple events. *Cuad. Investig. Geogr.* 44 (2) <https://doi.org/10.18172/cig.3344>.
- Holko, L., Danko, M., Slezák, P., 2020. Analysis of changes in hydrological cycle of a pristine mountain catchment. 2. Isotopic data, trend and attribution analyses. *J. Hydrol. Hydromech.* 68, 192–199.

- Jung, H., Koh, D.-C., Kim, Y.S., Jeon, S.-W., Lee, J., 2020. Stable isotopes of water and nitrate for the identification of groundwater flowpaths: a review. *Water*. <https://doi.org/10.3390/w12010138>.
- Krogh, S.A., Scaff, L., Kirchner, J.W., Gordon, B., Sterle, G., Harpold, A., 2022. Diel streamflow cycles suggest more sensitive snowmelt-driven streamflow to climate change than land surface modeling does. *Hydrol. Earth Syst. Sci.* 26, 3393–3417. <https://doi.org/10.5194/hess-26-3393-2022>.
- Leach, J.A., Laudon, H., 2019. Headwater lakes and their influence on downstream discharge. *Limnol. Oceanogr. Lett.* 4, 105–112. <https://doi.org/10.1002/lol2.10110>.
- Lee, J., Feng, X., Faiia, A., Posmentier, E., Osterhuber, R., Kirchner, J., 2010. Isotopic evolution of snowmelt: a new model incorporating mobile and immobile water. *Water Resour. Res.* 46. <https://doi.org/10.1029/2009WR008306>.
- López-Moreno, J.I., Vicente-Serrano, S.M., Moran-Tejeda, E., Zabalza, J., Lorenzo-Lacruz, J., García-Ruiz, J.M., 2011. Impact of climate evolution and land use changes on water yield in the ebro basin. *Hydrol. Earth Syst. Sci.* 15. <https://doi.org/10.5194/hess-15-311-2011>.
- López-Moreno, J.I., Gascoïn, S., Herrero, J., Sproles, E.A., Pons, M., Alonso-González, E., Hanich, L., Boudhar, A., Musselman, K.N., Molotch, N.P., Sickman, J., Pomeroy, J., 2017. Different sensitivities of snowpacks to warming in Mediterranean climate mountain areas. *Environ. Res. Lett.* 12. <https://doi.org/10.1088/1748-9326/aa70cb>.
- López-Moreno, J.I., Pomeroy, J.W., Alonso-González, E., Morán-Tejeda, E., Revuelto, J., 2020. Decoupling of warming mountain snowpacks from hydrological regimes. *Environ. Res. Lett.* 15. <https://doi.org/10.1088/1748-9326/abb55f>.
- López-Olmedo, F., González Menéndez, L., Rodríguez Fernández, L.R., Salazar Rincón, Á.E., Díez Herrero, A., Rubio Pascual, F.J., Luengo Olmos, J., Rábano Gutiérrez del Arroyo, I., 2020. Parque Nacional de la Sierra de Guadarrama: guía geológica. [In Spanish: Sierra de Guadarrama National Park: Geological Guide]. Ed. CSIC - Instituto Geológico y Minero de España (IGME). Madrid, 282pp. ISBN: 978-84-9138-102-0.
- Lundquist, J.D., Cayán, D.R., 2002. Seasonal and spatial patterns in diurnal cycles in streamflow in the Western United States. *J. Hydrometeorol.* 3, 591–603. [https://doi.org/10.1175/1525-7541\(2002\)003<0591:SASPID>2.0.CO;2](https://doi.org/10.1175/1525-7541(2002)003<0591:SASPID>2.0.CO;2).
- Morán-Tejeda, E., Lorenzo-Lacruz, J., López-Moreno, J.I., Rahman, K., Beniston, M., 2014. Streamflow timing of mountain rivers in Spain: recent changes and future projections. *J. Hydrol.* 517. <https://doi.org/10.1016/j.jhydrol.2014.06.053>.
- Musselman, K.N., Addor, N., Vano, J.A., Molotch, N.P., 2021. Winter melt trends portend widespread declines in snow water resources. *Nat. Clim. Change* 11, 418–424. <https://doi.org/10.1038/s41558-021-01014-9>.
- Niewodnizański, J., Grabczak, J., Barański, L., Rzepka, J., 1981. The altitude effect on the isotopic composition of snow in high mountains. *J. Glaciol.* 27, 99–111. <https://doi.org/10.3189/S0022143000011266>.
- Palacios, D., de Andrés, N., Luengo, E., 2003. Distribution and effectiveness of nivation in Mediterranean mountains: Peñalara (Spain). *Geomorphology* 54, 157–178. [https://doi.org/10.1016/S0169-555X\(02\)00340-9](https://doi.org/10.1016/S0169-555X(02)00340-9).
- Penna, D., Ahmad, M., Birks, S.J., Bouchaou, L., Brencić, M., Butt, S., Holko, L., Jeelani, G., Martínez, D.E., Melikadze, G., Shanley, J.B., Sokratov, S.A., Stadnyk, T., Sugimoto, A., Vreča, P., 2014. A new method of snowmelt sampling for water stable isotopes. *Hydrol. Process.* 28, 5637–5644. <https://doi.org/10.1002/hyp.10273>.
- Simpkins, G., 2018. Snow-related water woes. *Nat. Clim. Change* 8, 945. <https://doi.org/10.1038/s41558-018-0330-7>.
- Sturm, M., Goldstein, M.A., Parr, C., 2017. Water and life from snow: a trillion dollar science question. *Water Resour. Res.* <https://doi.org/10.1002/2017WR020840>.
- Tague, C., Grant, G.E., 2009. Groundwater dynamics mediate low-flow response to global warming in snow-dominated alpine regions. *Water Resour. Res.* 45. <https://doi.org/10.1029/2008WR007179>.
- Toro, M., Granados, I., Robles, S., Montes, C., 2006. High mountain lakes of the Central Range (Iberian Peninsula): regional limnology & environmental changes. *Limnetica* 25 (1), 217–252. <https://doi.org/10.23818/limn.25.17>.
- Viviroli, D., Dürr, H.H., Messerli, B., Meybeck, M., Weingartner, R., 2007. Mountains of the world, water towers for humanity: typology, mapping, and global significance. *Water Resour. Res.* 43. <https://doi.org/10.1029/2006WR005653>.
- Winkler, D.E., Butz, R.J., Germino, M.J., Reinhardt, K., Kueppers, L.M., 2018. Snowmelt timing regulates community composition, phenology, and physiological performance of Alpine plants. *Front. Plant Sci.* 9, 1140. <https://doi.org/10.3389/fpls.2018.01140>.
- Woelber, B., Maneta, M.P., Harper, J., Jencso, K.G., Gardner, W.P., Wilcox, A.C., López-Moreno, I., 2018. The influence of diurnal snowmelt and transpiration on hillslope throughflow and stream response. *Hydrol. Earth Syst. Sci.* 22, 4295–4310. <https://doi.org/10.5194/hess-22-4295-2018>.
- Yang, Y., Xiao, H., Wei, Y., Zhao, L., Zou, S., Yang, Q., Yin, Z., 2012. Hydrological processes in the different landscape zones of alpine cold regions in the wet season, combining isotopic and hydrochemical tracers. *Hydrol. Process.* 26, 1457–1466. <https://doi.org/10.1002/hyp.8275>.
- Yélamos, J.G., Sanz-Pérez, E., Escavi-Fernández, J.I., 2019. Las aguas subterráneas del Parque Nacional de la Sierra de Guadarrama. *Bol. Geol. Min.* 130, 743–772. <https://doi.org/10.21701/bolgeomin.130.4.009>.