

ADVANCED REVIEW

Understanding snow hydrological processes through the lens of stable water isotopes

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Snowfall may have different stable isotopic compositions compared with rainfall, allowing its contribution to potentially be tracked through the hydrological cycle. This review summarizes the state of knowledge of how different hydrometeorological processes affect the isotopic composition of snow in its different forms (snowfall, snowpack, and snowmelt), and, through selected examples, discusses how stable water isotopes can provide a better understanding of snow hydrological processes. A detailed account is given of how the variability in isotopic composition of snow changes from precipitation to final melting. The effect of different snow ablation processes (sublimation, melting, and redistribution by wind or avalanches) on the isotope ratios of the underlying snowpack are also examined. Insights into the role of canopy in snow interception processes, and how the isotopic composition in canopy underlying snowpacks can elucidate the exchanges therein are discussed, as well as case studies demonstrating the usefulness of stable water isotopes to estimate seasonality in the groundwater recharge. Rain-on-snow floods illustrate how isotopes can be useful to estimate the role of preferential flow during heavy spring rains. All these examples point to the complexity of snow hydrologic processes and demonstrate that an isotopic approach is useful to quantify snow contributions throughout the water cycle, especially in high-elevation and high-latitude catchments, where such processes are most pronounced. This synthesis concludes by tracing a snow particle along its entire hydrologic life cycle, highlights the major practical challenges remaining in snow hydrology and discusses future research directions.

This article is categorized under:

Science of Water > Hydrological Processes

Science of Water > Methods

KEYWORDS

ablation, isotopic lapse rate, stemflow, throughfall, wind redistribution

1 | INTRODUCTION

Seasonal snow covers 47 million km² or 30% of the Earth's land surface, with 98% of this cover located in the Northern Hemisphere, specifically in North America and Eurasia (Brodzik & Armstrong, 2017; Robinson, Dewey, & Heim, 1993). In fact, more than 50% of North America and Eurasia are seasonally snow covered. Snow is thus a key element of both the Earth's

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hydrological cycle and its surface energy balance (Frei et al., 2012). Depending on the different meteorological conditions, the temporary accumulation of water in the form of snow shifts daily, seasonally, and annually, from the period when precipitation falls as snow to the period when water is released via sublimation and melting. In the year 2000, around one sixth of the World's population was living in places with snow-dominated water resources and with low artificial water storage capacity, that is, using water resources heavily reliant on the natural water storage capacity of snow (Barnett, Adam, & Lettenmaier, 2005).

The dynamics of snow accumulation, storage, and melting play a major role in hydrological, ecological, and geomorphological processes (Chen, Liang, Cao, He, & Wang, 2015) and for domestic, industrial, and agricultural water use (Barnett et al., 2005), as well as for hydropower production (Schaeffli, 2015). Additionally, snowmelt can be a key driver of hydrological hazards (Chen et al., 2015), such as spring floods (Blöschl et al., 2017), summer droughts, and rain-on-snow (ROS) events (Freudiger, Kohn, Stahl, & Weiler, 2014). Snowmelt is also a primary temperature control for snow-influenced streams, with ensuing regulations on aquatic ecosystems (Fossheim et al., 2015) and on heat inputs to lakes and oceans (Lammers, Pundsack, & Shiklomanov, 2007; Yang, Marsh, & Ge, 2014).

The natural storage of water as snow is undergoing severe changes in a warming climate (Beniston et al., 2017; Brown & Mote, 2009). In a warmer world, the percent of precipitation falling as snow and the seasonal duration of that snow cover will likely decrease (Choi, Robinson, & Kang, 2010; Steger, Kotlarski, Jonas, & Schär, 2013). Snow may start melting earlier, thus shifting the corresponding timing and magnitude of river runoff peaks (Barnett et al., 2005). Somewhat counter intuitively, rates of snowmelt are also expected to decrease (Musselman, Clark, Liu, Ikeda, & Rasmussen, 2017).

Any change in this seasonal duration—or “snow cover phenology”(Chen et al., 2015)—has potentially important effects for water storage dynamics in mountain environments with permanent snow cover (Huss et al., 2017) in polar regions (Bokhorst et al., 2016), in low-elevation mid-latitude snow covers (Nolin & Daly, 2006), and in general for any water resources system heavily relying on the temporal storage of water in the form of snow (Barnett et al., 2005).

Snow is certainly among the most dynamic hydrological water stores (Sturm, 2015). According to Frei et al. (2012), the “accumulation and rapid melt (of snow) are two of the most dramatic seasonal environmental changes of any kind on the Earth's surface.” Compared with subsurface water storage, the presence and depth of a snowpack is far easier to estimate using remote-sensing (Frei et al., 2012) or ground-based techniques (Lundberg, Granlund, & Gustafsson, 2010). Estimating the actual water content of a snow cover in terms of its snow water equivalent (SWE; Jonas, Marty, & Magnusson, 2009) remains, however, challenging (Dozier, Bair, & Davis, 2016; Jonas et al., 2009). Detailed insights into snow accumulation and melt processes are difficult to obtain, given the generally harsh meteorological conditions prevailing in snow-dominated environments that make data collection very challenging.

Accordingly, we are still far from having a complete picture of how the temporary accumulation of water in the form of snow influences the catchment-scale water balance (Berghuijs, Woods, & Hrachowitz, 2014) or how its melting is partitioned into water flow paths according to their associated time scales (Musselman et al., 2017).

Stable isotope compositions of oxygen and hydrogen in water (subsequently referred to as stable isotopes of water) have a long-standing tradition as tracers in hydrology (Bowen & Good, 2015), which among many applications have been widely used to separate different sources of streamflow (Klaus & McDonnell, 2013), to understand hillslope-scale hydrologic processes (Tetzlaff, Birkel, Dick, Geris, & Soulsby, 2014) and to estimate the residence time of water at various catchment scales (Benettin et al., 2017; Birkel & Soulsby, 2015; Tetzlaff et al., 2015). For snow hydrology, such measurements are particularly promising because winter precipitation falling as snow generally has distinct isotopic compositions compared to summer precipitation, meaning it may be used to trace the evolution and contribution of snow to hydrological pathways within catchments.

In this review, the aim is to provide a comprehensive overview of the state of knowledge concerning how stable isotope compositions of water can be applied to further understand snow hydrology. This is done by:

- (1) Providing an overview of the snow regions of the world, to place the snow hydrological studies into a geographic context across the globe.
- (2) Outlining the fundamentals of stable isotope variations, and the spatiotemporal variations in isotope compositions of precipitation, where snow represents the solid phase.
- (3) Providing an in-depth analysis of how snow operates in the hydrological cycle, and how stable isotope measurements have contributed to these interpretations.
- (4) Examining the current state of knowledge concerning changes in the isotopic composition of snow during its hydrological life cycle.
- (5) Highlighting the significance of these findings for interpreting snow contributions to overall hydrological partitioning and fluxes.
- (6) Suggesting avenues for future research using stable isotope compositions in snow hydrology.

2 | SNOW REGIONS OF THE WORLD

In this paper, the focus is on understanding snow hydrological processes related to (sub)seasonal accumulation and release of snow in mountainous and high-latitude environments. This excludes polar regions that have permanent snow and ice cover (glaciers) and also cryospheric processes related to formation of firn and ice. Globally, seasonally snow-influenced regions are located in mountainous areas, mostly at latitudes greater than 45° North and South (Figure 1), except in regions influenced by maritime climates in Europe, the Pacific Northwest and British Columbia, where moisture converges from warmer ocean currents (Barnett et al., 2005).

The relative amount of precipitation falling as snow in snow-influenced regions depends on the intra-annual precipitation variability and the relationship between precipitation seasonality and the annual air temperature cycle (Willmott, Rowe, & Mintz, 1985; Woods, 2009). Ratios of relative snowfall vary strongly worldwide (Figure 1b). Similarly, the storage dynamics (i.e., the building-up, transformation, and ablation or mass reduction) of snow cover (see Section on *Usage of stable water isotopes to understand snow processes*) vary strongly from place to place, resulting in shallow cold snowpacks in the tundra or in relatively deep and warm snowpacks in maritime locations. Sturm, Holmgren, and Liston (1995) proposed a seasonal snow cover classification system with seven phenomenological classes, *tundra*, *taiga*, *alpine*, *maritime*, *prairie*, *ephemeral*, and a special “*mountain*” class, and related these classes to cold season climate variables (e.g., temperature, precipitation, and wind speed). Such a classification certainly has potential to transfer snow hydrological process understanding from one landscape to another, but as yet has found limited application in the hydrological literature (see Fayad et al., 2017a; Liston, 2004).

For this review, it is useful to consider fundamental regional differences in incoming and outgoing snow-water fluxes, in particular: (a) the seasonality of the snowfall period with respect to the melting period (occurring simultaneously or shifted in time) and (b) the main driver of snow ablation, either melt or sublimation or both. While only examples are given and not an extensive classification of the world's snow-influenced regions and mountain ranges, these two factors should be kept in mind as we explore isotopes in snow hydrology research. This is particularly important given that fundamental climatic differences might occur within relatively small areas, for example, at different elevations within a given mountain range.

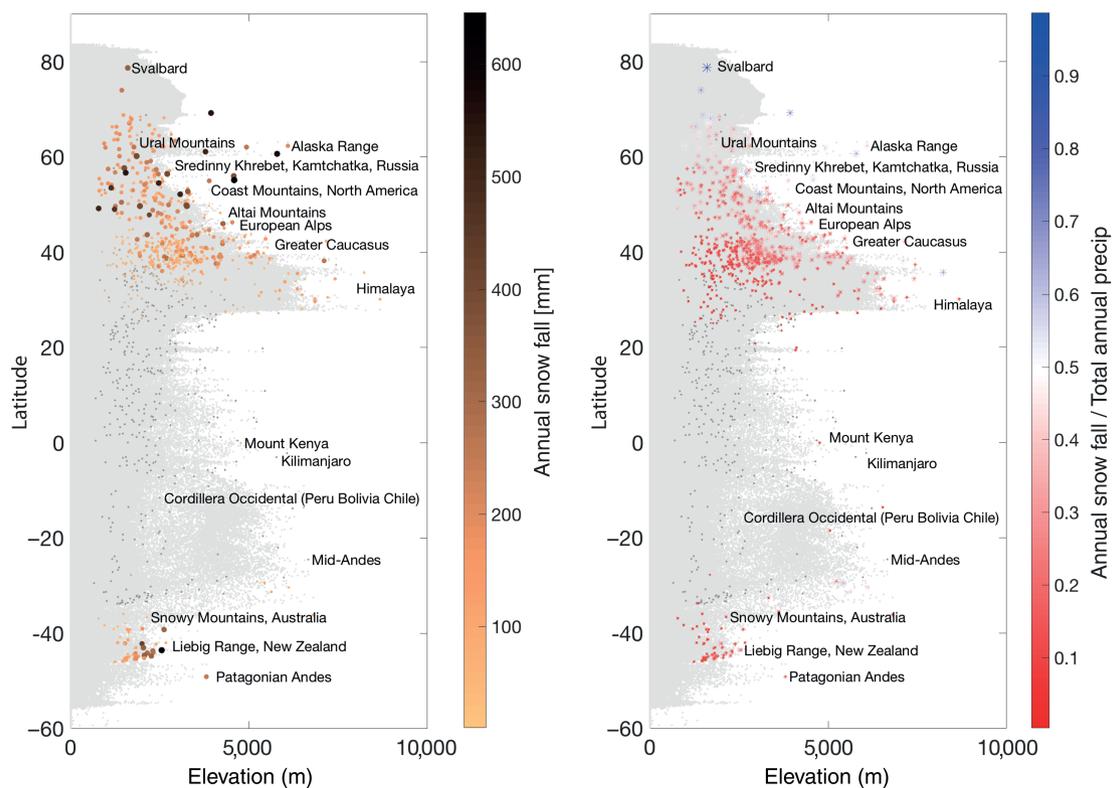


FIGURE 1 Amount of annual snowfall and ratio of snowfall to annual precipitation in world's mountain ranges; monthly snowfall computed with the equation proposed by Legates and Willmott (1990) from monthly precipitation and monthly temperature of the WorldClim data base (Hijmans, Cameron, Parra, Jones, & Jarvis, 2005); mountain ranges extracted with the mountain shape files provided by Körner et al. (2017), shown are the latitude of mid points and peak elevation; peak elevation obtained from the elevation dataset (called “alt” file) from the WorldClim data set. Dark gray dots correspond to mountain ranges without snowfall, light gray shading indicates all pixels in the WorldClim dataset. Colored dots on the left and colored asterisks on the right figure represent mountains with snow, with the marker size proportional to annual snowfall in the left figure and proportional to ratio of annual snowfall to annual precipitation in the right figure. The readers are referred to the electronic version for an enlarged version of the figure

Most snow-influenced regions and mountain ranges have a distinct snowfall (cold) and snowmelt (warm) season. This applies especially to all northern hemisphere high-latitude regions, the North American and Canadian mountain ranges, the European and the Japanese Alps, and to almost all seasonally snow-influenced mountain ranges in the Southern hemisphere. An exception is the temperate Cordillera in Peru and Bolivia that has a dry cold season (see the map of Peel, Finlayson, and McMahon (2007)) and, accordingly, snow accumulation and melt both occur during summer on high mountain peaks (Wagnon, Ribstein, Kaser, & Berton, 1999). The Himalaya is the most prominent example of a mountain range where there is a major overlap between the snowfall and snowmelt seasons (during the monsoon season (Kaser, Grosshauser, & Marzeion, 2010)) because the cold season is too dry for snow to accumulate. However, some areas of the Hindu-Kush Karakoram Himalayan region can receive a higher fraction of cold precipitation (Palazzi, von Hardenberg, & Provenzale, 2013), and some areas can have an alpine-like snow season (e.g., the Himachal Pradesh). In general, any region with a distinct dry cold season will be both accumulating and melting snow within the warmer season. A special case is that of dry mountains with sporadic snowfall that is retained due to generally cold temperatures, such as in the very high elevation but largely arid Andes (MacDonell, Kinnard, Molg, Nicholson, & Abermann, 2013). Sublimation plays a key role in snow ablation, occurring year-round under the influence of solar radiation and wind (Ayala, Pellicciotti, MacDonell, McPhee, & Burlando, 2017; Gascoin, Lhermitte, Kinnard, Bortels, & Liston, 2013). In general, sublimation is a potentially important driver of snow ablation in drier climates (see, for example, the review on Mediterranean snow hydrology by Fayad et al. (2017b)), and in cold and windy climates (due to the stronger sublimation of blowing snow (Law & Vandijk, 1994)), for example, in many high-elevation and high-latitude regions such as the Canadian Rocky Mountains (MacDonald, Pomeroy, & Pietroniro, 2010). Sublimation is typically also high in cold climate forests due to the easier sublimation of canopy intercepted snowfall (Pomeroy, Gray, Hedstrom, & Janowicz, 2002).

3 | BACKGROUND OF ISOTOPE HYDROLOGY

The basic concepts of how H and O isotopes are used in hydrology are summarized following Galewsky et al. (2016). In nature, hydrogen exists as two stable isotopes (^1H , ^2H or D) and oxygen as three stable isotopes (^{16}O , ^{17}O , ^{18}O) with the isotopologue (same molecule but with different isotopic composition) H_2^{16}O being the most abundant, followed by H_2^{18}O , H_2^{17}O , $\text{H}_1\text{D}^{16}\text{O}$.

H_2^{18}O (or ^{18}O) and HD^{16}O (or ^2H) are the most commonly used natural tracers in isotope hydrology. Accordingly, in this review, we only include studies using $^2\text{H}/^1\text{H}$ and/or $^{18}\text{O}/^{16}\text{O}$.

Isotopic values are expressed as a ratio (R) of concentration of heavier to lighter isotopes ($^2\text{H}/^1\text{H}$ or $^{18}\text{O}/^{16}\text{O}$) and standardized relative to the Vienna Standard Mean Ocean Water (VSMOW2) by the International Atomic Energy Agency (IAEA). The hydrogen or oxygen isotope composition of a sample, R_{sample} , ($^2\text{H}_{\text{sample}}/^1\text{H}_{\text{sample}}$ or $^{18}\text{O}_{\text{sample}}/^{16}\text{O}_{\text{sample}}$), is expressed using the so-called δ notation in units of per mil (‰), as

$$\delta^{18}\text{O} \text{ or } \delta^2\text{H} = \frac{R_{\text{sample}} - R_{\text{VSMOW}}}{R_{\text{VSMOW}}} \times 1,000. \quad (1)$$

The majority of precipitation originates from ocean evaporation, a process that preferentially samples the lighter isotopologues of water. Accordingly, the ratio of the Vienna standard, R_{VSMOW} , is generally higher than the ratio of any meteoric water sample and reported δ -values of such waters are mostly negative. Samples with higher (or less negative) $\delta^2\text{H}$ or $\delta^{18}\text{O}$ values have a greater proportion of heavier isotopes and are referred to as *more enriched in heavier isotopes*. Similarly, samples with lower (or more negative) $\delta^2\text{H}$ or $\delta^{18}\text{O}$ values compared to seawater have a smaller proportion of heavier isotopes and are referred to as *more depleted in heavier isotopes*.

During a phase change process (such as condensation, evaporation, etc.), fractionation changes the relative abundance of heavier and lighter isotopes in the two phases. Depending on the process, fractionation can take place under equilibrium conditions (equilibrium fractionation) or in nonequilibrium conditions (kinetic fractionation). At equilibrium, the forward and backward reaction rates of the phase change are identical. A typical example of equilibrium fractionation is condensation, where heavier isotopes are preferentially incorporated in the condensate, leaving the remaining vapor more depleted in heavier isotopes (Clark & Fritz, 1997; Kendall & McDonnell, 1998). However, during kinetic fractionation, the forward and backward reaction rates of the phase change are different. A typical example of kinetic fractionation is evaporation. During evaporation, both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the vapor phase decrease, whereas the remaining liquid becomes proportionately more enriched in the heavier isotopes of H and O, hence increasing the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values. In contrast to condensation, which is generally an equilibrium process, the kinetic effect is stronger for changes in $\delta^2\text{H}$ compared with $\delta^{18}\text{O}$ of the vapor phase as the HD^{16}O molecule is lighter than the H_2^{18}O molecule.

Given $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are both modified by mass dependent fractionation processes and are part of the same water molecule undergoing transformation, global precipitation follows a linear relationship $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$, which is called the global meteoric water line (GMWL; Craig, 1961). The intercept of the GMWL is referred to as *d-excess* (deuterium-excess factor) and is useful in distinguishing equilibrium and nonequilibrium processes (see hereafter) (Dansgaard, 1964; Galewsky et al., 2016). However, the slope and the intercept of precipitation samples at a given location might vary from the values of the GMWL, depending on the source of precipitation water (ocean water or local moisture recycling by terrestrial evaporation or plant transpiration). Hence, local meteoric water lines (LMWL or MWL) are used to describe the relationship between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ at a given location. Any deviation from the MWL gives insights into nonequilibrium processes such as evaporation, sublimation, and so forth at the given site.

During an equilibrium process (e.g., condensation), the isotopic values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ vary along the MWL (Figure 2). During a nonequilibrium process (e.g., evaporation), the isotopic values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ no longer vary along the MWL because of differential enrichment in ^2H and ^{18}O in the liquid phase. This results in evaporation processes having a different slope in their $\delta^2\text{H}$ - $\delta^{18}\text{O}$ relationship compared to equilibrium or condensation processes that typify atmospheric precipitation. During evaporation, the $^1\text{H}^2\text{H}^{16}\text{O}$ isotopologue of water, which is lighter than the $^1\text{H}^1\text{H}^{18}\text{O}$ isotopologue, is preferentially vaporized leaving the remaining liquid more enriched in heavier isotopologues of water (i.e., $^1\text{H}^1\text{H}^{18}\text{O}$, variants with ^{17}O are not considered here). This leads to the local evaporation line (LEL), which reflects the isotopic ratio of the remaining liquid (and not the evaporated vapor). The LEL has a slope (typically between 3 and 6) and a *d-excess* value lower than that of the MWL (Rose, 2003), meaning higher proportion of heavier isotopes of oxygen than hydrogen in the remaining liquid (Figure 2). Projecting the isotope values of evaporated water on the MWL by retracing its path along the LEL provides an estimate of the initial isotopic composition of water, provided there is no subsequent mixing (Rose, 2003). During summer, rain samples can also fall off the MWL and follow the LEL due to evaporation of the water droplets during their transit from the cloud to the ground (Winograd, Riggs, & Coplen, 1998).

The temperature at which an air mass condenses (cloud condensation temperature) influences the fractionation that occurs when precipitation forms, which determines its original stable water isotope ratio. Fractionation factors between vapor and liquid or vapor and solid (ice) decrease with increasing temperature (Akers, Welker, & Brook, 2017; Friedman, Redfield, Schoen, & Harris, 1964). Accordingly, higher air temperatures (positively correlated with cloud condensation temperature) lead to lower fractionation factors. As a result, precipitation forming at higher air temperatures is more enriched in heavier isotopes than precipitation forming at lower air temperatures.

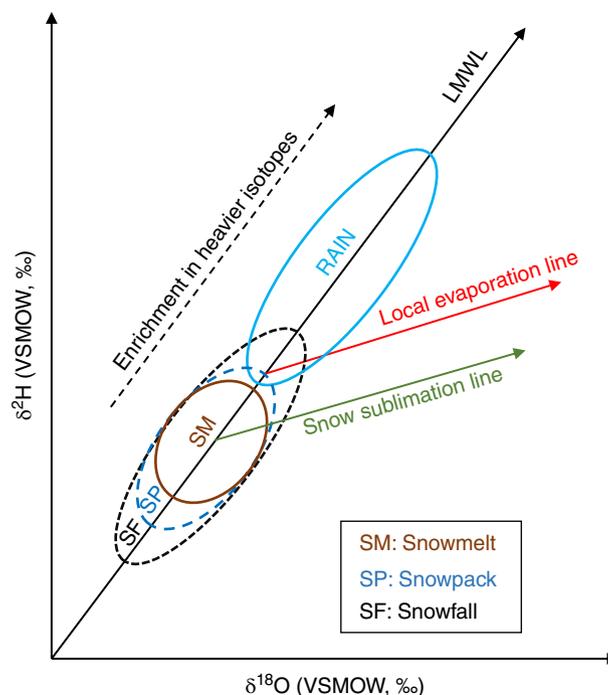


FIGURE 2 Conceptual representation of possible sample positions in the dual isotope space (formed by $\delta^2\text{H}$ and $\delta^{18}\text{O}$) for snow and rainfall samples from an entire hydrological year

At the beginning of a precipitation event, heavier isotopes are preferentially sampled out of the cloud as rain/snow. During the course of the event, precipitation becomes more depleted in heavier isotopes. This is also called the *rain-out effect* and it generally follows the Rayleigh distillation law during continued condensation (Good, Noone, Kurita, Benetti, & Bowen, 2015; Schürch, Kozel, Schotterer, & Tripet, 2003). Controls on the isotopic composition of precipitation due to elevation gradients (isotopic lapse rates) and air temperature (due to seasonality) are described in the section below.

3.1 | Elevation gradients and isotopic composition of precipitation

As moist air masses uplift (adiabatically) along a mountain range, condensation occurs at lower temperatures, which is also known as the *lapse rate* (Friedman, Smith, Gleason, Warden, & Harris, 1992; Galewsky et al., 2016; Winograd et al., 1998). The isotopic composition of precipitation varies systematically with elevation, becoming in general more depleted in heavier isotopes as rain out increases with elevation. Accordingly, this effect is called the *isotopic lapse rate*. Lower cloud condensation temperatures with increasing elevation also increase the isotopic fractionation between vapor and liquid, further increasing heavy isotopes in the residual air mass (Friedman et al., 1964). As condensation is an equilibrium process, the isotopic fractionation follows the MWL. An example of this effect is shown in the change of the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values measured as part of the GNIP (Global Network of Isotopes in Precipitation) network of stations across an elevation gradient in Switzerland (Figure 3). Here, the average isotope composition of precipitation shifts by $1.9\text{‰}/100\text{m}$ for $\delta^2\text{H}$ and $0.27\text{‰}/100\text{m}$ for $\delta^{18}\text{O}$, noting that in winter, above around 800 m asl, the precipitation is dominated by snow (Marty, 2008). Some version of this isotopic lapse rate is seen in almost all mountainous environments except on the leeward or “rain-shadow” side of mountains, which receive precipitation from clouds that have already passed over the highest elevation of the ridge and are no longer continuing to rise, keeping the cloud condensation temperature relatively stable (Bershaw, Penny, & Garzzone, 2012; Dietermann & Weiler, 2013; Koeniger, Hubbart, Link, & Marshall, 2008; Moran, Marshall, Evans, & Sinclair, 2007; Wen, Tian, Weng, Liu, & Zhao, 2012; Winograd et al., 1998). Moran et al. (2007) reported positive isotopic lapse rates (enrichment in heavier isotopes with increasing elevation) in snow samples on the leeward side of a glacierized valley in the Canadian Rockies (refer to Figure 4 in Moran et al. (2007)), which may occur only if the warmer temperatures and hence smaller vapor–liquid or vapor–ice isotopic fractionation factors offset the “rain-out” effect.

A number of studies around the world have reported on the effect of isotopic lapse rates of precipitation in streamwater (Jeelani, Saravana Kumar, & Kumar, 2013; Wen et al., 2012), groundwater (Lambán et al., 2015; O'Driscoll, DeWalle,

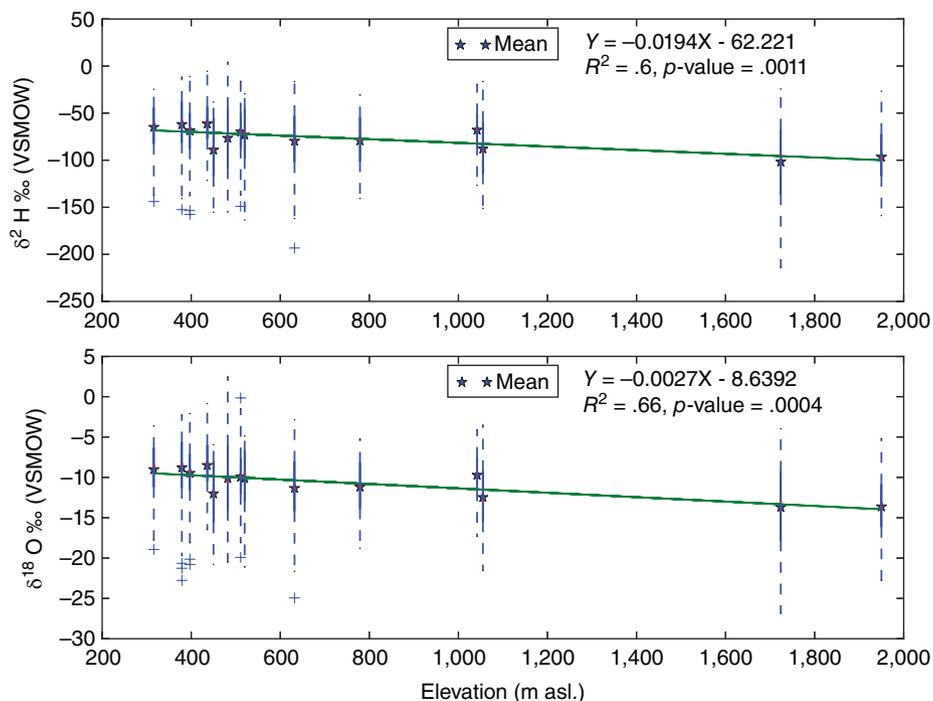


FIGURE 3 Variation of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in precipitation samples as a function of elevation, as collected by the GNIP (Global Network of Isotopes in Precipitation) network of gauging stations in Switzerland (data from 1966 to 2014). Snowfall is widespread during winter at elevations >800 m asl. (Marty, 2008)

McGuire, & Gburek, 2005), and soil water (O'Driscoll et al., 2005). However, this effect can be masked by other fractionating processes as well as elevation-dependent recharge processes. In the case of snow, ablation processes such as sublimation and melting change the isotopic compositions of existing snowpacks. This is especially apparent when isotopic lapse rates are calculated by sampling snow cores along an elevation gradient.

In the Ötztal Alps in Austria, Moser and Stichler (1974) proposed reversed isotopic lapse rates due to the enrichment of surface snow with heavier isotopes due to sublimation and melting processes. Zongxing et al. (2015) also showed reversed isotopic lapse rates in snowfall in the lower elevation (3,400–4,000 m) region of Shiyi Glacier (Tibetan Plateau). However, regular isotopic lapse rates were again seen at higher elevations (4,000–4,680 m). In this case, enrichment in heavier isotopes in the snowpack due to evaporation and sublimation along with snow drift from higher to lower elevations explained the reverse isotopic lapse rates. Additionally, the air mass trajectory can also mask the role of isotopic lapse rate as was shown in the Southeastern desert in California (USA) (Friedman et al., 1992).

3.2 | Seasonality in isotopic composition of precipitation

Precipitation isotopic composition depends on cloud condensation temperature (Friedman et al., 1964), which is intrinsically linked to the ambient air temperature. Owing to the seasonality in air temperature, isotopic compositions also globally show strong seasonality (Friedman et al., 1992; Lambán et al., 2015) (see an example in Figure 4). This seasonality in the isotopic composition is strongly linked to the aforementioned rain-out effect. In colder air masses, more water condensates than in warmer air masses, which leads to stronger depletion in heavy isotopes. Accordingly, precipitation forming in cold air masses is also more depleted in heavy isotopes than precipitation forming in warmer air masses. This explains the general tendency of rainfall being more enriched in heavier isotopes than snowfall at a given location.

The isotope lapse rates can also show seasonality with different lapse rate values at different times of the year. O'Driscoll et al. (2005) found in three catchments in Pennsylvania (USA) (elevations ranging from 225 to 740 m) a strong seasonality in isotopic lapse rates, with some months even showing positive slopes (enrichment in heavier isotopes with increasing elevation). They attributed this to different sources of cloud vapor at different times of the year, and to different synoptic drivers. However, it is rare to obtain positive isotopic lapse rates. It is important to note that Pennsylvania is very flat with the highest elevation less than 750 m, so the same physical processes might not be applicable in the other high elevation regions in the world like the European and Chilean Alps, the Himalayas, and so on.

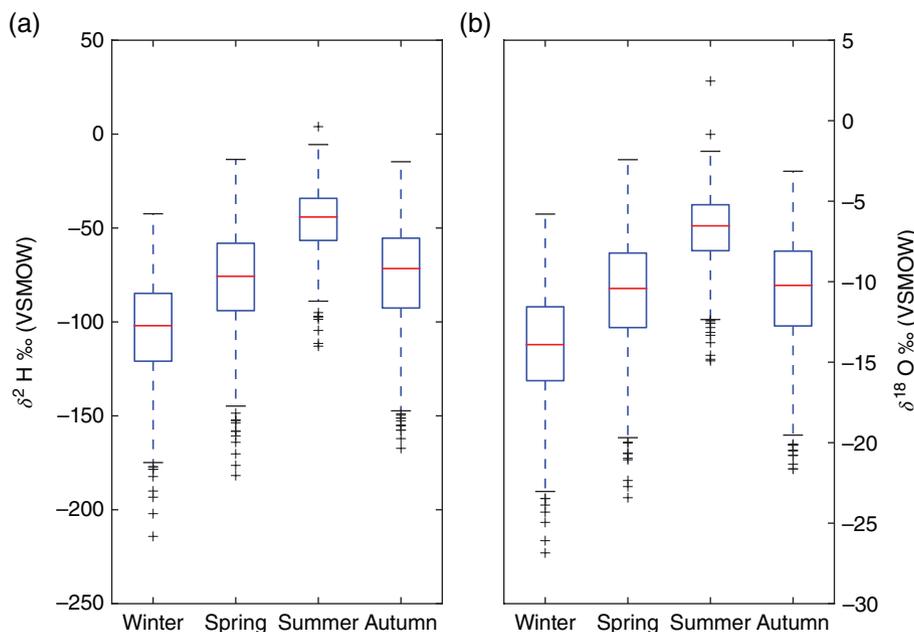


FIGURE 4 Seasonal variation of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in precipitation samples collected by the GNIP (Global Network of Isotopes in Precipitation) network of gauging stations in Switzerland (data from 1966 to 2014). The red line in the middle of each box shows median value, the box corresponds to the difference between third and first quartile values, whisker length is 1.5 times of the interquartile range and the points beyond the whiskers represent outliers

4 | GENERAL OVERVIEW OF SNOW IN THE HYDROLOGICAL CYCLE

When precipitation falls as snow, it enters a cycle of snow accumulation, redistribution, and ablation (mass reduction) via sublimation and melt (see Figure 5 and the textbook of Dingman (2002) for an overview of snow hydrological processes). Snow that accumulates on the ground under freezing conditions undergoes permanent snow metamorphism (change of snow grain size and shape due to vapor exchange, heat flow and pressure; Colbeck, 1982) and vapor exchange with the atmosphere. Accordingly, most snowpacks are distinctly layered, including the formation of structurally weaker layers (e.g., depth hoar layers), which are particularly relevant for avalanche formation (Gaume, Chambon, Eckert, & Naaim, 2013). Snowmelt water then either refreezes or leaves the snowpack if the local water retention capacity is reached, forming preferential meltwater flow paths (Katsushima, Yamaguchi, Kumakura, & Sato, 2013; Schneebeli, 1995). Substantial amounts of meltwater leave the snowpack only once the snowpack becomes *isothermal* (Dingman, 2002), which is when all the snowpack layers are at the same temperature (i.e., at the freezing point). Runoff generation from the melting snowpack occurs via direct surface runoff or via infiltration into the subsurface, resulting in groundwater recharge or in other flow processes in the subsurface (Wever, Comola, Bavay, & Lehning, 2017). Similar to purely rainfall driven infiltration, the rate of melt infiltration into the soil depends on the soil properties and in particular on its saturation state and hydraulic conductivity; frozen soil has an extremely small infiltration capacity but it is noteworthy that soil beneath a snowpack is not necessarily frozen (Wever et al., 2017) and that continuous (but low rate) snowmelt at the snow-soil interface is common in many places (Unnikrishna, McDonnell, & Kendall, 2002).

Redistribution of snow previously accumulated on the ground can occur via wind transport (Mott, Schirmer, Bavay, Grünwald, & Lehning, 2010) or avalanching, both of which can lead to considerable displacement of snow masses. Transport by wind typically leads to snow fragmentation (Comola, Kok, Gaume, Paterna, & Lehning, 2017), which favors snow sublimation from blowing snow (Essery, Li, & Pomeroy, 1999). Spatial precipitation patterns (orographic effects (Houze, 2012), seeder-feeder mechanisms (Choulaton & Perry, 1986)) together with preferential snow deposition (Lehning, Löwe, Ryser, & Raderschall, 2008) and wind redistribution leads to strongly heterogeneous snow accumulation patterns. Spatially variable snow ablation due to complex interactions with topography and vegetation further enhances the spatial heterogeneity of snow packs (Marks, Winstral, & Seyfried, 2002).

The presence of vegetation also affects snow processes through its modification of the surface energy budget (via the screening of solar radiation, emission of longwave radiation, thermal inertia, etc.). In forested areas, substantial amounts of snow can be intercepted by trees (Hedstrom & Pomeroy, 1998). Intercepted snow either returns as vapor to the atmosphere via sublimation or reaches the ground (soil or snowpack) via snow throughfall (TF) or snowmelt stemflow (STF).

These fundamental snow hydrological processes and pathways are illustrated in Figure 5 and are discussed in the following sections, including a detailed discussion of whether these processes are likely to change the isotopic composition of the snow.

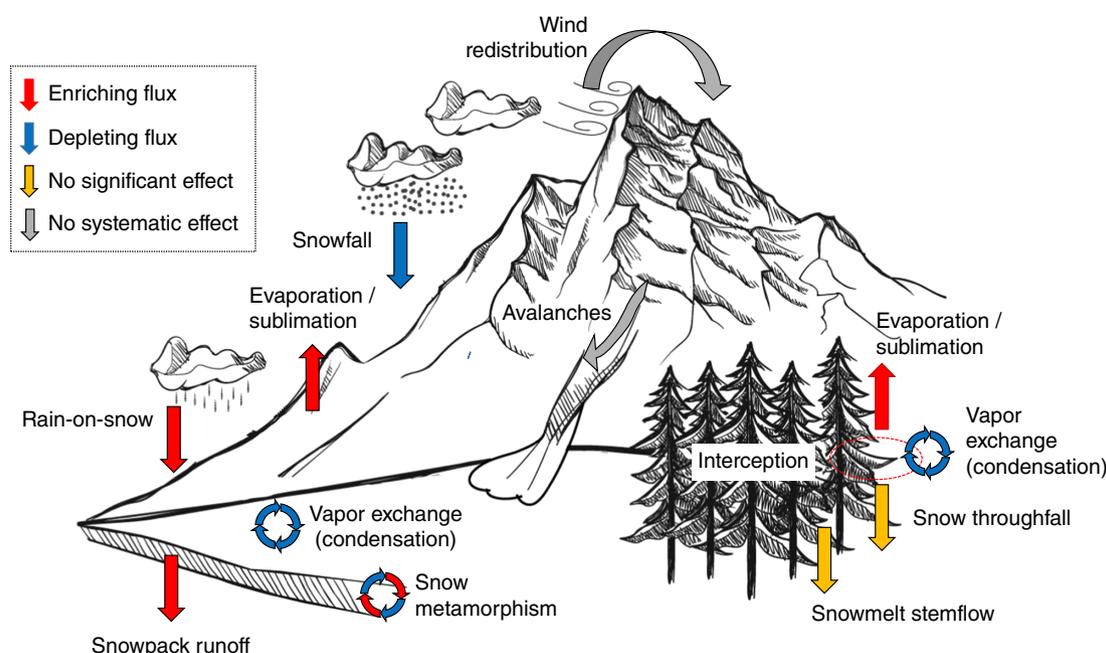


FIGURE 5 Life cycle of snow seen through the eyes of a hydrologist highlighting fluxes that lead to an enrichment or depletion in stable water isotopes of the snowpack (on the ground or intercepted by canopy); fluxes for which there is no systematic effect or no significant effect are also identified. (Graphic based on original work from www.freepik.com)

5 | EFFECTS OF SNOW HYDROLOGIC PROCESSES ON THE ISOTOPIC COMPOSITION OF WATER

The state-of-knowledge of the dominant processes that affect the isotopic composition of snow during its life cycle are further discussed below, starting with processes occurring at the canopy (interception and throughfall), at the snowpack-atmosphere interface (sublimation, vapor exchange) and within the snowpack itself (metamorphism, melt). A short discussion on the effect of snow redistribution on snowpack isotopic composition and an overview of dominant drivers of spatial heterogeneity of snow isotopes conclude this section.

5.1 | Interception and throughfall

Little work has been done to understand changes in the stable isotopic compositions of snow that is intercepted by the canopy (Allen, Keim, Barnard, McDonnell, & Renée, 2016; Claassen & Downey, 1995; Koeniger et al., 2008) or the subsequent transport to the ground via TF and STF. However, a number of studies have tried to model changes in TF on isotopic compositions by intercepted rain (Dewalle & Swistock, 1994; Gat & Tzur, 1967; Pearce, Stewart, & Sklash, 1986; Saxena, 1986; Uehara & Kume, 2012). A recent review by Allen et al. (2016) summarized rainfall interception processes and their effect on the stable isotopic composition of intercepted rain. Some of this discussion is useful to further understand potential effects on snow.

The canopy affects the isotopic composition of intercepted rain falling onto the ground via TF in three major ways: (a) Canopy evaporation enriches intercepted rain in heavier isotopes, where the degree of enrichment is a function of relative humidity. The majority of evaporation occurs from microdroplets created by rainfall splashes and the evaporation rate is accelerated by shear stress between the falling droplets and air (Murakami, 2006). (b) Isotopic exchange between canopy intercepted rain and surrounding vapor reduces variance, either by enriching or depleting the rain in heavier isotopes. In most instances, exchange leads to the progressive depletion of intercepted rain in heavier isotopes as the surrounding vapor is generally more depleted in heavier isotopes (Friedman, Benson, & Gleason, 1991). Unlike evaporation which is a kinetic process, exchange is an equilibrium process (Friedman et al., 1991) and the isotopic composition of intercepted rain remains on the MWL. (c) Selective canopy storage and transmission of rain to the ground as TF changes the isotopic composition of TF from bulk rain. For instance, if the canopy retains water at the end of a rain event which is more depleted in heavier isotopes (rain-out effect, refer to *Background of isotope hydrology* section), TF water will be more enriched than bulk rain. The residual intercepted water may also modify the isotopic composition of TF induced by the next storm, which may itself have a different isotopic composition depending on the vapor sources and its specific rain-out history. Canopy interception effects on the isotopic compositions (enrichment or depletion) are enhanced during smaller rain events (Soulsby, Braun, Sprenger, Weiler, & Tetzlaff, 2017) and in denser canopy stands (Allen et al., 2016).

To our knowledge, only Claassen and Downey (1995) and Koeniger et al. (2008) have explored changes in snow isotope composition via canopy interception, in Colorado (USA) and Idaho (USA), respectively. In the evergreen forests of Show-snow Mountain in Colorado (USA), snow accounts for more than 50% of annual precipitation, and interception of snow accounts for about half of the total snowfall. Claassen and Downey (1995) showed a high degree of enrichment in heavier isotopes of hydrogen (13‰) and oxygen (2.1‰) in the winter TF samples of intercepted snow, relative to the isotopic composition of fresh snow. The degree of enrichment depends on: (a) the residence time of intercepted snow (Claassen & Downey, 1995), (b) the size of the snowfall (Claassen & Downey, 1995), and (c) the density of forest canopy (Koeniger et al., 2008). (a) Longer residence time leads to more enriched TF and STF, as sublimation enriches the intercepted snow in heavier isotopes (Claassen & Downey, 1995). Clear sky conditions favor longer residence time of the intercepted snow, and hence more enrichment due to snow sublimation. However, air temperature might reduce the residence time of intercepted snow. When air temperature at the surface of intercepted snow approaches melting point, interception stops and a small amount of melt leads to a lubrication effect at the snow leaf interface, causing a large fraction of the intercepted snow to slide off. (b) The size of falling snow particles also characterizes the degree of isotopic enrichment, with smaller snow particles exhibiting greater enrichment in heavier isotopes (Claassen & Downey, 1995). (c) Higher degrees of enrichment are seen in denser forest canopies due to longer exposure of the intercepted snow to atmospheric drying (Koeniger et al., 2008).

5.2 | Snow sublimation

Sublimation is a kinetic (or nonequilibrium) fractionating process causing differential enrichment in the heavier isotopes of H and O (Earman, Campbell, Phillips, & Newman, 2006; Moser & Stichler, 1974; N'da et al., 2016; Ren, Yao, Yang, & Joswiak, 2013). Sublimation-induced changes on the isotopic composition of a snowpack are similar to the changes induced by evaporation on the isotopic composition of residual water (Earman et al., 2006). If a snowpack undergoes sublimation, the residual

snowpack isotopic composition follows the LEL with a reduced *d-excess* value (Figure 2; Ren et al., 2013; Stichler et al., 2001). It is interesting to note that snow sublimation during the trajectory of snowflakes from the cloud to the ground may not lead to substantial fractionation, presumably as it is an irreversible reaction (Friedman et al., 1992).

Snow sublimation is influenced by (a) vapor pressure deficit that is the difference in vapor pressure between surface snowpack layer and the surrounding air, (b) turbulent diffusion in air, (c) wind speed, and (d) solar radiation (Earman et al., 2006; N'da et al., 2016). Higher vapor deficit and solar radiation increase the rate of snow sublimation. Turbulent diffusion scales with wind speed, leading to an increase in the rate of snow sublimation. It is noteworthy that in Southwest USA, during periods of high solar radiation, melting is dominant and the snowpack isotope composition is governed by snowmelt (Earman et al., 2006). During periods of low solar radiation, evaporation and sublimation are the dominant controls on snowpack isotopic composition in Southwest USA (Earman et al., 2006).

Over the course of a day, if solar radiation and vapor pressure deficit are high, as they usually are in sunny and snowy conditions, sublimation from the top layer enriches the snowpack in heavier isotopes (Earman et al., 2006; Gustafson, Brooks, Molotch, & Veatch, 2010; Stichler et al., 2001). This is observable through snowpack *d-excess* values that decline faster over the course of the day (Moser & Stichler, 1974; Stichler et al., 2001) but remain constant during the night. At night, condensation of surrounding air moisture, which is more depleted in heavier isotopes, may compensate for the effects of daytime sublimation by increasing *d-excess* values (Moser & Stichler, 1974; Schlaepfer et al., 2014; Stichler et al., 2001). In the snowpacks in Rocky Mountains (USA), Schlaepfer et al. (2014) found no significant change in *d-excess* values over time and implied that sublimation may not always cause fractionation sufficient to influence the snowpack. However, in this case, it is also possible that the diurnal changes in the isotopic composition in the snowpack may mask the net isotopic effect of sublimation on the residual snowpack.

The isotopic effect of snow sublimation is restricted to the top layer of a snowpack (Moser & Stichler, 1974; Stichler et al., 2001). However, a sharp temperature gradient within a snowpack can initiate movement of water vapor from lower to upper layers, leading to mixing within different layers of the snowpack. Sublimation from the top layer can then sample water from the deeper layers. This was observed at the Fuji Dome station in Antarctica where during one period of the year, vapor from the lower snowpack layer moved to the surface and condensed (Motoyama, Hirasawa, Satow, & Watanabe, 2005). This was initiated by a sharp temperature gradient (about 3 °C) between the firn layer of the snowpack and surface air. Moser and Stichler (1974) in a laboratory experiment saw similar behavior. When a steep temperature gradient was induced, mass transfer took place from deeper snowpack layers to the surface.

Snow sublimation has also been shown to increase the *d-excess* of groundwater recharged via vapor condensation at higher elevations, from the vapor produced by sublimated snowpacks at lower elevation (Lambán et al., 2015). In a recent study of isotopic composition of 25 springs spanning elevations from 690 to 2,400 m in Ordesa and Monte Perdido National parks in Spain (karstic system) (Lambán et al., 2015), spring water had *d-excess* values higher than that of precipitation. Snow sublimation at low elevation had produced water vapor with a high *d-excess* that was lifted to higher elevations where it mixed with moisture from local sources and finally condensed. The majority of the springs were recharged from precipitation at higher elevations. Thus, the higher *d-excess* values in the condensed vapor propagated into the springs. The effect was more variable at higher elevations, observed by larger amplitude in $\delta^2\text{H}$ and in $\delta^{18}\text{O}$ values, than at lower elevations.

5.3 | Snow metamorphism and snowmelt

A snowpack is composed of solid, liquid, and vapor phases of water. Any exchange between the three phases can change the isotopic composition of the snowpack. Back in 1974, Moser and Stichler (1974) proposed that isotopic changes due to different snow processes (snowmelt, sublimation, metamorphism, etc.) are limited to the top layer of a snowpack and that the isotopic compositions of deeper layers remain, by and large, unaltered. However, subsequent studies (Friedman et al., 1991; Taylor et al., 2001; Unnikrishna et al., 2002; Winograd et al., 1998) found that snow metamorphism can also homogenize the whole snowpack. Taylor et al. (2001) noticed in snow samples collected in California that the variability in isotopic composition reduced, following the transitions from snowfall to snowpack and finally to snowmelt. Fresh snowfall had the highest variability in isotopic composition, which then reduced with deposition time as snow accumulated within the snowpack. Subsequent snowmelt from this snowpack had the lowest variability in isotopic composition (Cooper, 1998). Similar results were also reported in Alaska (Friedman et al., 1991) and in the Spring mountains in Nevada, USA (Winograd et al., 1998).

A number of processes can affect the isotopic composition of different layers within a snowpack. They have been summarized in a recent work on seasonal snowpacks in Idaho, USA (Evans et al., 2016). Water percolation within the snowpack (so-called pervasive flow), from snowmelt at the surface, induces a downward translation of the isotopic composition of the snowpack along the direction of the moving water particles. In contrast, mass loss due to snow sublimation from the snowpack surface shifts the isotopic composition of the snowpack upwards toward the snowpack surface. Diffusion and dispersion of water homogenizes the isotopic variance within the snowpack. A combination of diffusion and dispersion with either

pervasive flow or with sublimation shifts the isotopic composition downwards (toward the ground) or upwards (toward the snowpack surface), with some degree of homogenization within the snowpack. However, preferential flow of surface meltwater, either through macropores or through a sloped snowpack (commonly seen in mountainous regions), can release meltwater without affecting deeper snowpack layers (Eiriksson et al., 2013; Evans et al., 2016).

When the surface meltwater percolates through the snowpack, meltwater goes through cycles of crystallization and subsequent melt. Any meltwater that refreezes (crystallizes) enriches the solid phase of the snowpack in heavier isotopes, thereby depleting the residual meltwater in heavier isotopes. The heat released during crystallization can induce melting in adjacent layers of the snowpack. A number of models (Ala-aho et al., 2017; Feng, Taylor, Renshaw, & Kirchner, 2002; Lee, 2014; Lee, Feng, Faiia, Posmentier, Kirchner, et al., 2010; Lee, Feng, Faiia, Posmentier, Osterhuber, et al., 2010; Lee, Feng, Posmentier, Faiia, & Taylor, 2009; Taylor et al., 2001) have tried to characterize changes in the isotopic composition of snowpacks and of associated meltwater induced by snow metamorphism. It is important to note that redistribution within a snowpack but without mass loss does not change the bulk snowpack isotopic composition.

The isotopic composition within a snowpack is also affected by moisture exchange with the underlying soil. Friedman et al. (1991) observed that the bottom of snow cores was enriched in heavier isotopes compared with the bulk snowpack before the beginning of the melt season. This could not be explained by the stratigraphy resulting from different snowfall events during the accumulation period. The enrichment was due to (a) moisture exchange with the underlying soil layer caused by diffusive water transport from the more enriched soil into the snowpack and (b) fractionation due to crystallization (or condensation) of soil water into the snowpack. It is noteworthy that molecular diffusion of water vapor through a snowpack (either through advection up or down depending on the vapor pressure gradient) is a fractionating process.

Snowmelt that leaves the snowpack preferentially discharges isotopically light water, thereby enriching the residual snowpack in heavier isotopes (Ala-aho et al., 2017; Feng et al., 2002; Laudon, Hemond, Krouse, & Bishop, 2002; Shanley, Kendall, Albert, & Hardy, 1995; Soulsby, Malcolm, Helliwell, Ferrier, & Jenkins, 2000; Taylor et al., 2001; Taylor, Feng, Williams, & McNamara, 2002). It has been widely observed that early meltwater is more depleted in heavier isotopes and that, as the melt season progresses, both the residual snowpack and the generated meltwater become more enriched in heavier isotopes (Dietermann & Weiler, 2013; Taylor et al., 2001), which is also referred to as the *melt-out effect* (Ala-aho et al., 2017). To the best of our knowledge, the physical mechanisms of this melt-out effect are not well understood but likely involve the partial melting of snowpack which results in preferential loss of lighter isotopes in the early season meltwater.

Both meltwater rates and their isotopic composition show a strong diurnal variation, with higher snowmelt in the middle of the day due to stronger solar radiation. These higher melting rates provide less time for meltwater to remain in contact with solid phase water within the snowpack, which minimizes recrystallization and thus midday meltwater is more enriched in heavier isotopes (Taylor et al., 2001).

5.4 | Snow redistribution

Redistribution of snow either by wind transport (Mott et al., 2010) or avalanching (Schweizer, Bruce Jamieson, & Schneebeli, 2003) typically takes place over spatial scales from a few tens (wind) to hundreds of meters (Comola, 2017) (avalanching) and can involve significant amounts of snow mass redistribution. It does not have a systematic effect on the composition of snowpack isotopes. When an avalanche redistributes a large fraction of a snowpack from higher to lower elevations, the isotopic composition of the higher elevation snowpack is mixed, to some (and highly variable) extent, with the snowpack at lower elevations. Similarly, when wind blows snow from one place to another, the drifting snow carries the original isotopic composition with it, leading to mixing between snowpacks from distinct places. While this wind-induced mixing might have a significant effect around mountain ridges, the dominant wind effect on the isotopic composition is the enhanced sublimation of drifting snow, due to (a) snow fragmentation (Comola et al., 2017) and (b) enhanced evaporative demand of the atmosphere in presence of wind. Sublimation enriches the underlying snowpack in heavier isotopes (refer to section on *Snow Sublimation*) (Essery et al., 1999).

Thus, it is difficult to clearly state the net effect of wind and avalanche on the isotopic composition of snow, especially in complex terrains. In contrast, in flatter areas a more continuous snow drift from the surface layer can occur, and the corresponding enhancement of sublimation might result in a clear pattern in the isotopic composition of the snowpack, but this phenomenon has, to our knowledge not yet been studied.

5.5 | From the point to the catchment scale

The spatial variability of a snow cover and its isotopic ratios are driven by the temporal sequence of snow accumulation, redistribution, transformation, and ablation processes that vary strongly in space and whose dominance varies according to climate and topography. Understanding their joint effect on a catchment scale snowpack requires necessarily detailed local studies,

	Tundra	Taiga	Alpine	Maritime	Prairie	Ephemeral
Vapor exchange	→	▶	→	▶	•	•
Snow melt	→	→	▶	→	→	▶
Wind redistribution	▶	•	→	→	▶	•
Snow sublimation	▶	▶	→	•	▶	•

▶ Dominant process
→ Locally important
• Not as important

FIGURE 6 Dominant drivers of spatial isotopic heterogeneity according to the different snowpack types as defined by Sturm et al. (1995). Highlighted here is the relative importance of vapor exchange, snowmelt, wind redistribution, and snow sublimation in enhancing the isotopic heterogeneity of the final snowmelt beyond what was initially introduced by snowfall

including a characterization of the initial isotopic heterogeneity of snowfall and its subsequent evolution through time in the snowpack. Understanding isotopic heterogeneity at the catchment scale, and its impact on the isotopic signature of snowpack and snowmelt, necessarily begins with identifying the locally dominant processes that drive the isotopic ratios of a snowpack away from its initial snowfall ratios. The key processes that affect the isotopic spatial heterogeneity after initial snowfall are wind redistribution, vapor exchange, snow sublimation, and snowmelt. Their importance can be categorized for different snowpack types at different spatial scales. As an example, we propose in Figure 6 a classification of the dominant drivers of heterogeneity for the six global snowpack types proposed by Sturm et al. (1995) (Tundra, Taiga, Alpine, Maritime, Prairie, and Ephemeral). Such a classification of snowpack types and the associated driving processes at finer spatial scales can help in the identification of corresponding hydrological snowpack units (in analogy to hydrological response units (Gassman, Reyes, Green, & Arnold, 2007)), which might provide a way forward to characterize the isotopic composition of snow at the catchment scale. It is important to emphasize that these processes occur at a hierarchy of spatial scales (Clark et al., 2011), meaning it can be difficult to isolate the effects of individual processes on the isotopic ratios of snowpack and snowmelt. In addition, slope and aspect will play a role in the spatial heterogeneity of snowpack isotope evolution at hillslope to catchment scales, for example, through their influence on solar radiation, wind, and tree cover. This means a detailed analysis of individual processes at a point scale cannot necessarily account for all the complex spatial dynamics that may occur at the catchment scale. Ideally then, detailed point-scale snowpack and snowmelt information should be considered in the context of how spatially representative such conditions are expected to be within a given catchment (Box 1).

BOX 1

MODELING SNOWPACK ISOTOPE FRACTIONATION AND ISOTOPE RATIOS IN SNOWMELT

Stable isotope compositions of water have a great potential to constrain catchment-scale hydrological models that predict river streamflow as a function of incoming precipitation (see Birkel and Soulsby (2015) for a review). In the presence of snow, the use of stable water isotopes to improve a hydrological process model hinges on the ability to characterize snowmelt isotopic composition based on observed precipitation isotopes through the entire life cycle of snow. Only few studies have attempted to build such a complete model from precipitation to streamflow isotopes for snow-influenced catchments. One such example is the work of Ala-aho et al. (2017) who incorporated changes incurred in the isotopic composition of snow during its hydrologic life cycle, and coupled it with a snow process model. The key advancements were the fully distributed (spatially) and parsimonious nature of the model. This is a major step forward in tracer-aided hydrologic modeling (Birkel & Soulsby, 2015; Capell, Tetzlaff, & Soulsby, 2012; Delavau, Stednyk, & Holmes, 2017; McMillan, Tetzlaff, Clark, & Soulsby, 2012; Regan, Goodhue, Naughton, & Hynds, 2017; Stednyk, Delavau, Kouwen, & Edwards, 2013; Tetzlaff et al., 2015; Tunaley, Tetzlaff, Birkel, & Soulsby, 2017; van Huijgevoort, Tetzlaff, Sutanudjaja, & Soulsby, 2016a; van Huijgevoort, Tetzlaff, Sutanudjaja, & Soulsby, 2016b).

6 | FOCUS ON SELECTED SNOW HYDROLOGICAL PROCESSES

Below we present examples of how stable isotope composition can be used to unravel snow processes within the hydrological cycle. We focus on three topics that have received particular research focus in the recent past, (a) the effects of canopy on snowpacks, (b) ROS events, and (c) ground water recharge from snow.

6.1 | Canopy effects on underlying snowpack

Canopy cover affects the underlying snowpack by altering the SWE along with its isotopic composition (Biederman, Brooks, et al., 2014; Biederman, Harpold, et al., 2014; Gustafson et al., 2010; Koeniger et al., 2008). Koeniger et al. (2008) found that the snowpack in a forested watershed in Idaho (USA) was enriched in heavier isotopes due to enriched TF, caused by sublimation of the canopy intercepted snow and associated evaporation. Longer exposure time of the intercepted snow led to greater enrichment in heavier isotopes. Gustafson et al. (2010) investigated the effect of canopy shading on the isotopic composition of a snowpack in Jemez Mountain in New Mexico (USA). During the maximum snow accumulation period with similar winter precipitation, the snowpack in a nonshaded area showed greater enrichment in heavier isotopes than that under shade.

Another interesting use of isotopic variation to understand canopy interception processes was seen in the Central Rocky Mountains (USA) (Biederman, Brooks, et al., 2014; Biederman, Harpold, et al., 2014). A mountain pine beetle (MPB) infestation destroyed most of the tree canopy in the Central Rocky Mountains. The canopy formerly intercepted a large amount of snow, much of which sublimated before reaching the forest floor. After the infestation, less snow was intercepted due to reduced canopy, and the SWE of the underlying snowpack was expected to increase. However, Biederman, Brooks, et al. (2014) and Biederman, Harpold, et al. (2014) found SWE during maximum snow accumulation phase to be unchanged, despite small changes in winter precipitation. To answer this anomaly, Biederman, Brooks, et al. (2014) and Biederman, Harpold, et al. (2014) carried out a study in two headwater catchments in the region over the winters of 2011 and 2012. One of the catchments was MPB affected, while the other one was used as a control. In the MPB affected catchment, the underlying snowpack was enriched in heavier isotopes, supporting kinetic fractionation due to sublimation and accompanying evaporative loss. However, there was no change in the isotopic composition in snowpack of the unaffected catchment. Newly exposed forest floor due to MPB experienced more direct solar radiation, which increased direct sublimation and evaporative loss from the underlying snowpack. This enhanced sublimation from the snowpack was equivalent in quantity with sublimation from the snow intercepted by the canopy, hence keeping the total SWE constant. The variation in isotopes provided insight on the “invisible snow” processes that went undetected by simply monitoring snow volume.

6.2 | Rain-on-snow

ROS events can release amounts of water that are substantially higher than the actual rainfall amounts onto the preexisting snowpack. Such events can be associated with large flood events and are known to trigger landslides, change channel morphology by enhancing erosion processes and influence water quality (Brunengo, 1990; Guan, Waliser, Ralph, Fetzer, & Neiman, 2016; McCabe, Hay, & Clark, 2007; McCabe, Wolock, & Austin, 2016; Rössler et al., 2014; Singh, Spitzbart, Hübl, & Weinmeister, 1997; Surfleet & Tullos, 2013). The frequency of ROS peak flow events is projected to increase at number of places under a warming climate (Surfleet & Tullos, 2013). Given that rainfall has a different isotopic composition than the preexisting snowpack, stable water isotopes can be used to investigate two key characteristics of ROS events: (a) the origin of the water that is released during the event (rainfall vs. melted water that was stored in the snowpack) and (b) the flow paths and associated transmission times of the released water.

The amount of runoff induced by ROS events depends on the spatial extent and cold content of the snowpack prior to the onset of rain. Cold content represents the amount of energy needed to raise the entire snowpack to the 0 °C melting point. An isothermal snowpack is associated with higher temperature, higher density, and with larger crystal sizes. Such snowpacks are known to produce higher proportional runoff than snowpacks that are not isothermal. This comes from the fact that less additional energy from the incoming rainfall is required to heat the isothermal snowpack to 0 °C (Colbeck, 1975; Gerdel, 1945; Juras et al., 2016; Maclean, English, & Schiff, 1995). During a ROS event, radiation (Mazurkiewicz, Callery, & McDonnell, 2008), rain and turbulent exchanges with the atmosphere transport heat into the snowpack. As incoming rain percolates through the snowpack, refreezing occurs, which releases heat and increases the temperature of the snowpack. As a result, large amounts of water can be released from the snowpack, either infiltrating into the ground or running off directly into the stream. In contrast, in a nonisothermal snowpack, incoming heat is not as efficient at producing snowmelt and the snowpack can retain more liquid water on crystal surfaces and in the voids (Gerdel, 1945).

Stable water isotopes have been used to analyze these snowpack processes and ensuing water flow paths at the plot scale during artificially induced ROS experiments (a review is given in Juras et al. (2016)). Juras et al. (2016) showed for example with the help of $\delta^2\text{H}$ measurements that such an artificial ROS event in the Krkonoše mountains (Czech Republic) led to percolation of rain water through the snowpack, pushing old water out of the snowpack via a piston flow mechanism.

Several studies observing the evolution of the isotopic content of snowpacks during natural rainfall events noted that ROS-induced snowmelt leads to higher ratios of surface flow to total runoff, than subsurface flow. These results have been reported in the Sierra Nevada forests (USA) (Kattelmann, 1987), in the Central Adirondack Mountains (USA) (Burns & McDonnell, 1998), in headwater and suburban catchments in Ontario (Canada) (Buttle, Vonk, & Taylor, 1995; Maclean et al., 1995; Wels, Taylor, Cornett, & Lazerte, 1991), and in the Krkonoše mountains (Czech Republic) (Juras et al., 2016).

TABLE 1 Summary of studies estimating groundwater recharge from summer (rain) and winter precipitation (snow), along with the used snow end member, that is, snowfall or snowmelt or a combination of the two

Authorship	Year (isotopes used)	Location	Summary	Snow end member
Simpson et al. (1970)	1968–1969 ($\delta^2\text{H}$, $\delta^{18}\text{O}$)	Arizona (USA)	Winter runoff dominant in groundwater recharge (numerical estimates not provided)	Snowmelt
Maule et al. (1994)	1986–1987 ($\delta^2\text{H}$, $\delta^{18}\text{O}$)	Alberta (Canada)	Approximately 44% groundwater recharge due to winter precipitation (~21% of annual precipitation) (fractionation corrected estimates)	Snowfall
Winograd et al. (1998)	1966–1988 ($\delta^2\text{H}$, $\delta^{18}\text{O}$)	Spring mountains, Nevada (USA)	Approximately 90% groundwater recharge due to snow (~66% of annual precipitation)	Snowfall and Snowmelt
Rose (2003)	1999–2002 ($\delta^2\text{H}$, $\delta^{18}\text{O}$)	Four sites in Sierra Nevada (USA)	>90% groundwater recharge due to winter precipitation (75–80% of annual precipitation)	Snowfall and Snowmelt
O'Driscoll et al. (2005)	1999–2000 ($\delta^{18}\text{O}$)	Three catchments in Pennsylvania (USA)	Approximately 90% groundwater recharge due to snow (~66% of annual precipitation)	Snowmelt
Earman et al. (2006)	2002–2004 ($\delta^2\text{H}$, $\delta^{18}\text{O}$)	Four sites in South Western United States (USA)	40–70% groundwater recharge due to snow (25–50% of annual precipitation)	Snowfall and Snowmelt
Kohfahl et al. (2008)	2004–2005 ($\delta^2\text{H}$, $\delta^{18}\text{O}$)	Granada basin (Spain)	Recharge predominantly due to winter rain and melting snow	Snowfall and Snowmelt
Penna, Engel, et al. (2014)	2011–2013 ($\delta^2\text{H}$, $\delta^{18}\text{O}$)	Saldura catchment, Eastern Italian Alps (Italy)	Seasonal variation in groundwater recharge due to snowmelt with annual contribution varying from $(58 \pm 24\%$ to $72 \pm 19\%)$	Snowfall and Snowmelt
Jasechko et al. (2014)	Metadata study		Isotopes and global hydrologic model suggest dominant winter precipitation recharge in temperate and arid climates and suggest wet season bias in tropical regions	Snowfall
Jasechko and Taylor (2015)	Metadata study		Preferential recharge of groundwater from heavy storm in the tropics	Rainfall
Zappa et al. (2015)	2010–2013 ($\delta^2\text{H}$, $\delta^{18}\text{O}$)	Gudjareti (Georgia)	Winter precipitation is very important source of groundwater recharge	Snowfall and Snowmelt
Cervi et al. (2015)	2004–2008 ($\delta^{18}\text{O}$)	Mt. Modino area, northern Apennines (Italy)	Predominant recharge from winter and spring precipitation	Snowmelt
Herrera et al. (2016)	2004–2005 ($\delta^2\text{H}$, $\delta^{18}\text{O}$)	Andean alps (Chile)	Predominant groundwater recharge from winter precipitation	Snowfall
Jasechko et al. (2017)	1991–2012 ($\delta^2\text{H}$, $\delta^{18}\text{O}$)	Nelson river watershed (Canada)	Fraction of groundwater recharge by winter precipitation ~1.3–5 times that of precipitation during warm months	Snowfall
Penna et al. (2017)	2011–2015 ($\delta^2\text{H}$, $\delta^{18}\text{O}$)	Rio Vauz catchment, eastern Italian alps (Italy)	Recharge predominantly due to snowmelt ($64 \pm 8\%$)	Snowfall and Snowmelt

Interestingly, in two forested catchments in Ontario (Canada), Casson, Eimers, and Watmough (2014) found using streamflow isotopes that ROS-induced events were dominated by baseflow and not by surface runoff.

Overall, stable water isotopes have a high potential to provide insights into ROS events across a range of spatial and temporal scales. Given that ROS events typically result in a rapid hydrologic response, progress in terms of high-temporal resolution of isotopic observations will certainly yield new insights into snow hydrological processes across scales.

6.3 | Estimating the contribution of rain versus snow to streamflow and groundwater recharge using mixing models

In a warming climate, more precipitation is expected to fall as rain than as snow (Choi et al., 2010; Steger et al., 2013). This is likely to change the proportion of rain versus snow contributing to the outgoing fluxes, and potentially the magnitude of the fluxes, from catchments such as evapotranspiration, groundwater recharge, and runoff. Stable isotopes of water are commonly used as tracers to identify the proportion of rain versus snow contributions to these fluxes, especially runoff and groundwater recharge (Earman et al., 2006). This is because snow is generally more depleted in the heavier isotopes than rain (Figure 2), which allows samples of runoff or groundwater falling within the isotopic range between rain and snow “end members” to be assigned proportional contributions using a linear mixing model (Obradovic & Sklash, 1986).

An impressive number of studies (Cervi et al., 2015; Earman et al., 2006; Herrera et al., 2016; Jasechko et al., 2014; Jasechko & Taylor, 2015; Jasechko, Wassenaar, & Mayer, 2017; Jeelani, Bhat, & Shivanna, 2010; Kohfahl et al., 2008; Lechler & Niemi, 2012; Maule, Chanasyk, & Muehlenbachs, 1994; Mountain, James, & Chutko, 2015; O'Driscoll et al., 2005; Penna, Engel, et al., 2014; Penna et al., 2017; Rose, 2003; Simpson, Thorud, & Friedman, 1970; Winograd et al., 1998; Zappa et al., 2015) have used a stable isotope approach to attribute percentages of snow and rain as sources for annual groundwater recharge (see a summary in Table 1). In general, they found that the snowmelt yield to groundwater recharge per unit of

TABLE 2 Overview of the processes that can bias snow end member estimates in mixing models: Potential biases introduced when a linear mixing model is used to estimate snow proportions in streamflow or groundwater recharge derived from snow samples taken at different stages of the hydrologic cycle of snow; *scale* refers to the spatial scale at which the discussed bias is relevant, *places* refers to locations where the bias might be relevant

Sample type	Omitted process	Type of estimation bias	Scale	Places
Snowmelt	Spatial snowmelt heterogeneity	<i>Unbiased</i> if samples from all dominant flow generation locations <i>Biased</i> otherwise	Hillslope to catchment	Areas with spatially heterogeneous snow recharge or runoff generation (hotspots)
Snowpack	Time-variable isotope signal of snowmelt water	<i>Underestimated</i> if many early season snowpack samples <i>Overestimated</i> if samples from ripe snowpack only	Point to catchment	Areas with significant snow accumulation period
Snowfall	Snowpack evolution and melt	<i>Underestimated</i>	Point to catchment	Areas with significant snow accumulation period
Snowfall	Snowpack sublimation	<i>Underestimated</i>	Point to catchment	Areas with significant sublimation
Snowfall	Snow interception and related sublimation	<i>Underestimated</i>	Point to catchment	Areas with significant snow interception and sublimation
Snowfall/ Snowpack	Snow lapse rate	<i>Overestimated</i> if majority of samples from low elevation <i>Underestimated</i> if majority of samples from high elevation	Catchment	Area with large elevation range

precipitation is higher than that of rain-induced recharge. The dominance of snowmelt-induced groundwater recharge has been shown in the United States (Earman et al., 2006; O'Driscoll et al., 2005; Rose, 2003; Simpson et al., 1970; Winograd et al., 1998), in Canada (Jasechko et al., 2017; Maule et al., 1994; Mountain et al., 2015), in the Himalayas (Jeelani et al., 2010), in Switzerland (Halder, Decrouy, & Vennemann, 2013), in Spain (Kohfahl et al., 2008), in Georgia (Zappa et al., 2015), in Italy (Cervi et al., 2015; Penna, Engel, et al., 2014; Penna et al., 2017), and in Chile (Herrera et al., 2016). A recent analyses (Jasechko et al., 2014; Jasechko & Taylor, 2015) of published stable isotope data with the help of a global hydrologic model suggest that spring snowmelt due to winter precipitation dominates recharge in temperate and arid climates. In tropical regions of the world, where snowfall generally does not contribute to the overall water balance, the isotope approach revealed that majority of groundwater recharge occurred during heavy storm events (Jasechko & Taylor, 2015).

Earman et al. (2006), using $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values in the Southwestern United States, suggested two mechanisms behind snowmelt-dominated groundwater recharge: (a) During the snowmelt season in the Southwest United States, vegetation is still mostly dormant which leads to smaller losses by evapotranspiration than during the summer, allowing more time for meltwater to infiltrate, and recharge groundwater. (b) The summer storms in Southwest United States are high intensity, and short duration causing a higher proportion of overland flow. On the other hand, snowmelt in the Southwest U.S. is typically low intensity but long in duration, which gives more opportunity for infiltration and groundwater recharge.

This enhanced snow proportion in groundwater is a good explanation for the proportionally higher snow contributions to streamflow as noted in several studies (Li, Wrzesien, Durand, Adam, & Lettenmaier, 2017). This might especially be the case in higher elevation areas where shallow groundwater is critical for streamflow generation.

It is important to note that using stable isotope compositions of snowfall or from snowpack as a proxy for the meltwater recharging groundwater and supplying streamflow might result in a considerable bias of actual snow contributions (Earman et al., 2006; Lechler & Niemi, 2012; Pavlovskii, Hayashi, & Lennon, 2017). This can be understood within the dual isotope space, where groundwater and streamflow samples are usually located somewhere between rain and snow. Snowmelt samples are on average closer to groundwater and streamflow samples than snowpack or snowfall samples. Accordingly, a mixing model may underestimate the contribution of snowmelt to streamflow and groundwater recharge when computed with (uncorrected) snowfall or snowpack samples, instead of actual snowmelt samples. An overview of the processes that can bias snow end member estimates in mixing models is given in Table 2. In general, it is recommended to either use the stable isotope composition of snowmelt, or where this is not practical, to examine correcting for potential snowpack enrichment after snowfall, resulting from evaporative losses through sublimation and melt-out effects (Box 2).

7 | THE HYDROLOGICAL LIFE CYCLE OF SEASONAL SNOW—A SYNTHESIS

We can summarize the key steps in the isotopic evolution of snowfall, snowpack, and snowmelt as representative shifts in the dual isotope space over the course of a typical snow season (Figure 7). Fresh snowfall may fall directly on bare ground or pre-existing snow, or be intercepted by the canopy. The intercepted snow, and the top layer of fresh snow on the ground, will be subject to varying degrees of sublimative enrichment. The developing snowpack will therefore represent some mixture of unmodified, and isotopically enriched snow.

BOX 2

SNOWMELT ISOTOPE SAMPLING METHODS

Snowmelt samples are critical as water from snowmelt contributes significantly to groundwater recharge via infiltration and to streamflow via both surface and subsurface flow paths. However, obtaining representative snowmelt samples is difficult because of the spatial and temporal variability across snowpacks, requiring snowmelt measurements at a number of remote locations, typically at high elevations, which becomes a major technical challenge. This is why snowpack samples are often used as a substitute for snowmelt samples. The problem with this substitution is that stable water isotope measurements obtained from conventional snow coring methods do not necessarily yield a representative sample of the isotopic ratio of snowmelt that will leave the snowpack (Earman et al., 2006; N'da et al., 2016). Snow lysimeters are most commonly used to obtain snowmelt samples beneath the snowpack. Recently, a number of studies (Frisbee, Phillips, Campbell, & Hendrickx, 2010; Frisbee, Phillips, Campbell, Hendrickx, & Engle, 2010; Holko et al., 2013; N'da et al., 2016; Penna et al., 2014) have also recommended the use of passive capillary sampling procedures to sample meltwater at the base of a snowpack. The advantage of this method is obtaining a snowmelt sample without the potential water ponding that can occur with lysimeters, and thereby avoiding evaporative fractionation.

Over the course of a snow season, both the snowpack and snowmelt undergo three key phases of isotopic evolution. The first is during the longer period of snowpack accumulation, within which melting phases can still occur. These melt events flush the lighter isotopes, resulting in depleted meltwater and a proportionately enriched snowpack, which in combination is commonly referred to as the “*melt-out effect*.” However, the majority of snowmelt release typically occurs in a relatively shorter period of time (Woods, 2009) at the end of the snow season; and this is the most significant phase in terms of snow meltwater contributions to the catchment hydrological cycle. The rapid reduction in snowpack volume produces a well-mixed snowmelt that homogenizes the isotopic signal, and therefore reduces isotopic variance relative to the snowpack. Finally, the melting of minor amounts of residual snow patches at the very end of the season can produce highly variable isotopic compositions of snowmelt, albeit with a considerably lower total flux. This end-of-season variability results from isotopic enrichment of the residual snowpack due to sublimation, and limited mixing at low snowpack depths and volumes.

Given that snowfall is strongly depleted in heavier isotopes with respect to summer rainfall, the average isotopic composition of a snowpack will generally remain more depleted than summer rainfall throughout the accumulation and ablation season despite the enriching effect of snowmelt and sublimation (Figure 2). Accordingly, snowmelt runoff from seasonal snowpacks can be assumed to show a narrow range of isotopic compositions (compared to snowfall) especially during the main phase of snowpack melting. The average isotopic ratios of snowfall, snowpack, and snowmelt are statistically similar, which is also reflected in Figure 2. All this can be used in the context of mixing models to estimate source contributions, for example, for streamflow or groundwater.

In environments where sublimation is low, the snowmelt composition lies on the local meteoric water line; and conversely, any departure of snow samples from the meteoric water line can provide some insights into the importance of sublimation in a given environment.

8 | DIRECTIONS FOR FUTURE RESEARCH

In 1998, Kendall and McDonnell (1998) proposed the use of alternative tracers, other than the stable water isotopes of water (^2H and ^{18}O), to better understand snowmelt processes. These include using alternative tracers such as electrical conductivity, water temperature, anions, and cations. In the last decade, ^{17}O has been suggested as an additional tracer to better constrain the hydrologic cycle (Berman, Levin, Landais, Li, & Owano, 2013; Birkel & Soulsby, 2015; Galewsky et al., 2016). However, very little work has been done using ^{17}O in snow hydrology, largely related to the difficulty of routinely measuring the ^{17}O concentrations in water. It is now well known that ^{17}O is relatively insensitive to temperature, but sensitive to humidity (Angert, Cappa, & DePaolo, 2004; Berman et al., 2013). Due to differences in rates of molecular diffusivity between ^{17}O and ^{18}O , using *O17-excess* in addition to *d-excess* may help to better constrain kinetic processes such as evaporation and sublimation (from both intercepted snow and from the snowpack). To our knowledge, however, there are no studies using ^{17}O to better quantify snow sublimation or snowpack processes in general. Future research using all the three stable water isotopes (^2H , ^{17}O and ^{18}O) will certainly provide insights into the potential use of ^{17}O in snow hydrology.

Most of the work in snow isotope hydrology has focused on either estimating the proportion of snow and rain in streamflow and groundwater, or on the isotopic changes in snowmelt induced by snowmelt and sublimation. Much remains to be

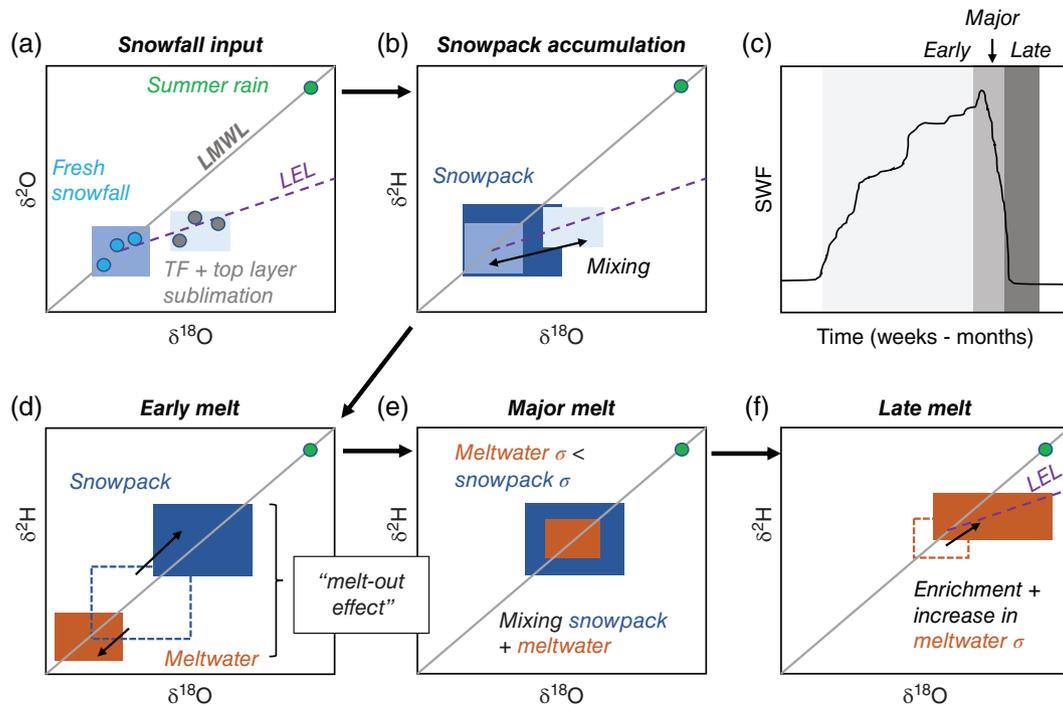


FIGURE 7 Tracking the evolution of snow isotopes from inputs of snowfall (a) to snowpack (b), and throughout the melting process (d–f). A representative temporal evolution of snowpack (represented as snow water equivalent) is provided in (c), highlighting the ranges over which early, major, and late melting phases and isotope changes are likely to occur. Plots b,d,e,f synthesize the isotopic evolution of snowpack and snowmelt from a “control volume” perspective, while (a) is from the perspective of a “pulse” of snowfall that could fall directly to the ground or be intercepted by the canopy and undergo isotopic modification due to sublimation (along the local evaporation line) and subsequent transport to the ground as snow throughfall (TF). The evolution of hypothetical samples (circles) and their ranges in dual isotope space (colored boxes) are shown in (a), with subsequent plots only showing the range as colored boxes. In subplot (e), σ represents the standard deviation of the meltwater or the snowpack sample

known on how canopy alters the isotopic composition of snow via interception, which is a substantial part of the water budget, especially in forested regions. The spatial variability in canopy interception is also understudied. Future research should focus on improving the spatial representation of stable water isotopes in intercepted snow and accumulated snowpack, and on understanding how this spatial heterogeneity translates into changes in the isotopic composition of the final meltwater.

Despite advancements in understanding isotopic evolution within seasonal snowpacks, there are very few studies that use them in predictive modeling to draw insights into the overall water budget. Examples on how to draw on isotope-based process understanding for snow hydrological modeling at the catchment scale are still rare. We hope that our synthesis encourages hydrologists to find new ways of constraining models with insights gained from stable isotope compositions of water.

9 | CONCLUSION

Snow undergoes significant changes from the time of its formation as precipitation to when it leaves the snowpack via sublimation or melt. These changes might not completely “overwrite” the stable water isotopic composition of the initial snowfall and, accordingly, research has been focused on understanding the isotopic composition of snow and its usefulness to track hydrological fluxes. We reviewed in detail the current knowledge of changes in the isotopic composition of snow across its entire hydrological life cycle. The effects on the isotopic composition of the different snow processes can be summarized as follows:

1. Variability in the isotopic composition of snow reduces from the onset of snowfall to the date of final snowmelt. Reduction in variance is caused by isotopic redistribution within the snowpack during the snow accumulation phase, in combination with other snow metamorphism processes.
2. Snowmelt during the early melt season is more depleted in the heavier isotopes which in due course of the melt season, becomes more enriched. Snowmelt isotopic compositions are correlated with melt rates, being more enriched in the heavier isotopes when melt rates are higher (typically during the day).

3. Snow interception can alter the isotopic composition of snow, from the time when snow first falls on the canopy to when it leaves the canopy and builds up on the ground. Longer snow residence times on the canopy are typically associated with higher degree of enrichment, especially when snow sublimation is significant.
4. The degree of canopy shading can substantially alter the isotopic composition of the underlying snowpacks. Snowpacks are more depleted in heavier isotopes in a well-shaded area, as their direct exposure to the solar radiation is small, leading to a smaller sublimation effect.
5. Snow sublimation enriches the isotopic composition of the residual snowpack in heavier isotopes. After enrichment, the remaining snowpack isotopes plot along the local evaporation (sublimation) line in the dual isotope space.
6. The fact that snow is isotopically lighter than rain can be leveraged to examine seasonal dependence of stream runoff or groundwater recharge.

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CONFLICT OF INTEREST

The authors have declared no conflicts of interest for this article.

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