Decomposing high-mountain streamflow by means of tracer-based monitoring and modelling

Dissertation

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Summary

Water of mountain regions has always been an important resource (e.g. drinking water, energy supply, irrigation) and a threat (e.g. flood, avalanche, debris flow) to people living in and close to mountain regions. Human-induced and environmental change likely force the hydrologic system to change, but reliable scenario simulations are hindered due to uncomplete understanding of hydrologic processes, particularly in glacierized high-elevation catchments. The input sources of streamflow (i.e. rainfall-, snowmelt-, and ice melt-derived components), as well as the flow paths and transit times of those components play a key role for the quantity and quality of water, but their understanding remains limited.

This thesis aims at reducing the outlined research gap by tracer-based monitoring and modelling and improves the understanding of hydrologic processes in glacierized high-elevation catchments under consideration of different system states. Therefore tracer-based mixing, surface energy-balance and tracer-aided hydrologic modelling methods were applied in the Rofental (Oetztal Alps, Austria) to reveal the ice melt, snowmelt and rain component of streamflow, their flow paths, as well as the catchment transit time and the subsurface storage potential.

A tracer-based mixing model (with oxygen-18) was combined with a snowmelt model to derive streamflow components of event (snowmelt) and pre-event water (mainly groundwater) at the event scale during a snow ablation period. In late April during the early melt period, 35% of streamflow comprised of snowmelt. High portions of snowmelt (75%) were estimated during the peak melt period in early June, when the pre-event water of the subsurface reservoir was already spilled and filled with same-season snowmelt water. A three-component mixing model using oxygen-18 and electrical conductivity (antecedent rain, new ice melt and old groundwater) was applied in a sub-catchment of the Rofental at the event scale during the glacier ablation period. The ice melt fraction was very variable according to the atmospheric conditions with maximum event fractions up to 69%. Contribution of antecedent rain from the subsurface was significant (16%), but old groundwater was the dominant fraction (49%) during the events. A surface energy-balance model was combined with a lumped parameter transit time model to investigate streamflow transit time and catchment subsurface storage during the period 2014 to 2017. High young (<3 months; 42%) and old water fractions (>5 years; 28%) characterized the age spectra of streamflow and indicated a highly non-linear streamflow tracer response as well as a high subsurface storage potential (14 m water equivalent) of the hydrogeological response units (moraines, talus, alluvium, rock glaciers, fractured bedrock).

A perceptual model of the main catchment functions was derived that describes the tracer and runoff response of the Rofenache and links it with the related hydrologic processes. This leads to the conclusion that high-mountain streamflow is not only the sum of surficial catchment input from rainfall, snowmelt and ice melt. Hence, closing the high-mountain water balance with regard to the hydrologic processes cannot reliably be done without accounting for the storage in and the delayed release of water from the subsurface.
Kurzfassung


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1 Introduction

1.1 On the importance of mountain water resources

The occurrence of water is subject to physical, chemical, biological and socio-economic processes. Water of mountain regions is, and has always been an important resource (e.g. drinking water, energy supply, irrigation, tourism) as well as a threat (e.g. flood, avalanche, debris flow) to people living in and close to mountain regions (Viviroli, 2018). In 2010, 10 % of the world population lived in mountain areas (IPCC, 2019), but this percentage did not include lowland population relying on mountain water resources. Furthermore, it is expected that by 2050 ~1.4 billion lowland inhabitants critically depend on mountain water (Viviroli et al., 2019). The cryosphere of high-mountain regions plays a major role therein, consisting of permafrost, snow cover and glaciers. Lake and river ice may play a minor role in most of the often steep and rugged catchments at the small scale (i.e. the headwater catchments). Due to climate change, the global mountain cryosphere is subject to severe recent and projected changes, both leading to system changes of the hydrologic system. The dynamic of permafrost, snow and glaciers thus control the volume, timing and biogeochemical characteristics of runoff (IPCC, 2019).

The high-mountain regions, such as the European Alps, are often referred to ‘water towers’ (Viviroli, 2018) with high amounts of high quality water supplying adjacent lowlands, e.g. up to more than 2.5 times water yield from mountain areas (Viviroli, 2018). Elevated precipitation amounts and delayed release of snowmelt and ice melt during the ablation period, especially during dry periods, support this terminology.

Observed changes of the mountain cryosphere are forced by atmospheric conditions and feedbacks (IPCC, 2019) resulting in a decreasing snowfall fraction of precipitation, earlier snowmelt and receding glaciers. There is evidence that some mountain regions are warming at an increased rate compared to lowlands (i.e. elevation-dependant warming; Pepin et al., 2015) leading to a non-uniform pattern at the global scale. The driving mechanisms and underlying physical processes cannot be fully explained by now (IPCC, 2019). This means, especially headwater catchments can experience dramatic influences, e.g. due to shifts in precipitation type (snow vs. rain). The observed changes of the mountain cryosphere propagate to the hydrologic system, resulting in alteration of timing, amount and biogeochemical characteristics of streamflow on a global scale (IPCC, 2019), for the European Alps (Beniston et al., 2018), for Austria (APCC, 2014) and for the Oetztal region (Hanzer et al., 2018; Hanzer et al., 2016). Further alteration in timing, amount and biogeochemical characteristics of streamflow is also projected for the future. Besides some regional differences, the mainly temperature-induced changes are mostly consistent throughout the above-mentioned regions and directly relate to the timing of yearly discharge maxima (e.g. earlier in the year), a transition of runoff regimes (e.g. glacial to nival) and an increase in winter runoff, all three having considerable impact on water usage, such as for hydropower plants, drinking water supply, agriculture and tourism. Increased release of heavy metals such as mercury or nickel was observed in alpine lakes,
rivers and from rock glacier outflow (e.g. Engel et al., 2019). Future increase in heavy metal concentrations can further threaten the general high quality of many mountain water resources.

1.2 Tracer-hydrology of headwater catchments

Hydrologic features
The headwater catchments of mountain regions, although a subjective definition, typically feature 1st and 2nd order streams and are the main suppliers for downstream water users. They are mainly decoupled from human interferences and often have an undisturbed near-natural character. This makes them appropriate for basic scientific research. Regarding the main function of the hydrologic system, i.e. the partitioning, storage and release of water within the catchment boundaries (Wagener et al., 2007), glacierized high-elevation catchments feature some extraordinaire attributes: A high fraction of precipitation falls typically as snow, leading to the storage in the snowpack at the seasonal scale and as firn or glaciers at the annual to decadal scale. This water is released attenuated in response to atmospheric forcing when large energy amounts are available, producing typical diurnal variation and annual peaks (Fountain and Tangborn, 1985; Hock, 2005). Further storage is obtained in the subsurface by soil, moraines, talus, rock glaciers, valley floors and in some catchments even in fractured bedrock (Hayashi, 2019). Evapotranspiration is often reduced due to the cold climate and large fractional area above the tree and the snow line, favouring effective infiltration due to snowmelt (Jasechko et al., 2017). Input source components of streamflow are rain, ice melt and snowmelt, all of them flowing by various paths to the stream and the outlet. These include surface and subsurface flow paths: channel flow (fast to very fast), overland flow (fast), interflow (fast and slow) as well as shallow (slow) and in some larger catchments even deep groundwater flow (very slow).

One must take in mind that the definition of streamflow components can lead to a misunderstanding when applying different methods and models. The differing nature of streamflow components are dictated by the method or model used to quantify the river discharge components. These can either i) be components originating from source areas (e.g. from glacier area including snowmelt, ice melt and rain), ii) be processes of runoff generation (e.g. overland flow) or iii) be input source components (e.g. ice melt) (Weiler et al., 2018). The velocity of the water particle dictates the tracer concentration in streamflow, whereas the celerity, or propagation of wave speed, controls the hydrologic response of the stream (McDonnell and Beven, 2014). Therefore velocity is always slower than celerity in catchment hydrology. Tracers can help to unravel transit times of water through the catchment or residence time of water in an aquifer (Hrachowitz et al., 2016; McGuire and McDonnell, 2006). The transit time is related to storage (discharge × transit time equals storage). The mixing of runoff components can occur in an aquifer or conceptual model store completely or partially (with limited mixing volume). Considering numerical modelling nomenclature, the latter is termed ‘effect tracking’ while the first is called ‘particle tracking’ (Weiler et al., 2018).
Tracers

Tracers can be grouped into two basic categories: 1) Artificial tracers are added intentionally to hydrologic systems at a limited temporal and spatial scale (Leibundgut and Seibert, 2011). A prominent example is the salt dilution method to measure discharge by applying sodium chloride as a tracer. 2) Environmental tracers can be utilized at the catchment scale and their input is provided by natural processes (e.g. precipitation; Leibundgut and Seibert, 2011). A comprehensive overview of tracers in hydrology can be found in Leibundgut et al. (2011). Environmental tracers have supported to disentangle many of the scientific challenges in catchment hydrology since the 1960s; e.g. early work on hydrograph separation from Pinder and Jones (1969). Two environmental tracers are relevant in this thesis: the ratio of the rare oxygen-18 to the abundant oxygen-16 isotope ($^{18}$O/$^{16}$O) and electrical conductivity (EC).

Oxygen-18 is a stable water isotope and its global abundance is 0.2 % (Mook, 2001). As part of the water molecule, the ‘built-in’ tracer is ideal to follow the path of water throughout the hydrologic cycle by leaving a distinct fingerprint. The $^{18}$O/$^{16}$O ratio can be measured with cavity ring-down spectroscopy (CRDS) and is reported with the delta notation in per mil ($\delta^{18}$O) relative to the Vienna standard mean ocean water (VSMOW). This often results in lower values (negative values) of meteoric water compared to VSMOW in the mid-latitudes. A basic overview of isotope methodology is provided by Mook (2001) or Clark and Fritz (1997). The precision of CRDS measurements is very good, typically below 0.1 ‰ (1 standard deviation.). The different water pools (e.g. snow vs. rain) often have distinct isotope ratios, a result of the temperature-dependant fractionation processes (Urey, 1947) which leads to higher fractionation factors at low temperatures. The resulting temperature effect (Dansgaard, 1964) is a powerful tool with many applications in hydrology, e.g. the stable isotope thermometer (Dansgaard, 1964). Fractionation within the hydrologic system occurs mainly due to phase changes which lead to a change in the isotope ratios of the product and the reactant. The heavier isotope ($^{18}$O) therefore typically concentrates in the denser phase, whereas the lighter isotope ($^{16}$O) concentrates in the less dense phase. Changes in isotope ratios can also occur due to mixing processes. Tracer masses are conserved during mixing of two compounds which allows for further applications in hydrology such as the application of mixing models for hydrograph separation (e.g. Pinder and Jones, 1969). Several effects are described for isotope ratios of precipitation, the so-called Dansgaard effects (Dansgaard, 1964). Most important to this study is the altitude effect, i.e. a decrease in the isotope ratio of water sources (e.g. precipitation) by elevation. This is driven by a combination of adiabatic cooling (temperature effect) and moisture depletion (a Rayleigh-type distillation process; Leibundgut et al., 2011). Global mean values for $\delta^{18}$O typically vary between 0.1 and 0.36 ‰ per 100 m (Leibundgut et al., 2011).

EC is a physico-chemical sum parameter of water, often strongly correlated with the amount of total dissolved solids (Hayashi, 2004). Its value is given in microsiemens per centimetre ($\mu$S/cm) and describes the ease of electrical current to pass through water, typically for a reference temperature of 25 °C. The higher the value, the more charged ions are dissolved in the liquid, allowing more electrical current to pass. The measurement is fast and inexpensive, making it an ideal tool for high-frequency analyses. EC is a surrogate for water chemistry and is useful for e.g. identifying hydrologic processes or separating runoff components (Can-
Paoli et al., 2019; Richards and Moore, 2003). EC of water input into catchments is controlled by dry deposition of aerosols (e.g. dust) and wet deposition of precipitation (moisture origin, air quality). The latter is probably more important for the hydrologic system and can be influenced by natural (e.g. salt spray) and anthropogenic factors (e.g. industrial emissions). EC of surface and subsurface water can then further be increased or decreased, as in the case of snow and ice (i.e. solute flush; Fountain, 1996), typically resulting in very dilute water (Tranter, 2005). The increase in EC depends on the solubility of the material (i.e. weathering process) and is controlled by the residence time (or contact time) and temperature. An elevation effect can be ascribed to the decrease in weathering rates at higher elevations (Drever and Zobrist, 1992).

Applications
Studies of $\delta^{18}$O and EC have been conducted in high-elevation catchments with varying degree of glacier cover worldwide to i) separate streamflow into its components by mixing models that solve the mass balance of water and tracer fluxes, and to ii) identify flow paths of water and dominant streamflow-generating processes. The most recent catchment studies were conducted in the European Alps (e.g. Zuecco et al., 2019), in high-mountain Asia (e.g. Williams et al., 2016), or in the American Cordillera (e.g. Rodriguez et al., 2016). The gathering and interpretation of $\delta^{18}$O and EC data are dictated by the spatio-temporal tracer variability of respective end-members. Here, the term ‘end-member’ refers to any potential water source that can contribute to streamflow. The outlined spatio-temporal variability entails uncertainty which propagates to the results of the mixing model. A main methodological challenge is to separate the hydrograph into multiple spatio-temporal components (pers. comm. with Jeff McDonnell, August 2015).

The seasonal cycle of $\delta^{18}$O in precipitation is often very pronounced (due to the temperature effect described above). Water age distribution (or age components) of streamflow can be inferred from its attenuation in the output signal (dampening effect) by e.g. applying the convolution integral method (McGuire and McDonnell, 2006) or by comparing amplitude ratios of input and output cycles (Kirchner, 2016a, b). High-elevation catchment studies were mainly conducted in snowmelt-dominated regions (mostly non-glacierized or with only very small glacier coverage of a few percent; Seeger and Weiler, 2014; von Freyberg et al., 2018). Water age and liquid water storage studies (storage here not considered as snow and ice) are very rare for glacierized areas, although the storage capabilities of high-mountain catchments are recently identified by Staudinger et al. (2017) for Swiss catchments and reviewed by Hayashi (2019) at the global scale. The unknown transit time distribution of many hydrologic compartments is also one of the ‘23 unsolved problems in hydrology’ (Blöschl et al., 2019) which applies particularly to glacierized high-elevation catchments.

1.3 Aims and outline of this thesis
The scientific advancement of hydrology, such as improved understanding of the hydrologic processes in glacierized high-elevation catchments, is dictated by new measurements, new analyses and new modelling approaches (Blöschl et al., 2019). The overall research aim of this
thesis is to better understand the hydrologic functioning of glacierized high-elevation catchments under consideration of different system states. Based on the overall research aim, this thesis explores high-mountain streamflow dynamics by considering the coupled hydrologic and tracer response of streamflow to climate forcing under consideration of different system states during rainfall-, snowmelt- and ice melt-dominated periods. This PhD work addresses some of the manifold and complex environmental processes in the test catchment Rofental (Oetztal Alps, Austria) by tracer-based monitoring and modelling. Therefore the environmental tracers $\delta^{18}O$ and EC were utilized since they provide insights into the water sources at the catchment-scale. The specific research objectives of this thesis are

- the investigation of snow and ice melt spatio-temporal tracer variability at various scales
- the quantification of discharge components, and
- the estimation of streamflow transit time and catchment subsurface storage.

Chapter 1 is the general introduction to the scientific research objectives of this thesis. The PhD work has been conducted in the test catchment Rofental: its characteristics, as well as the particular hydro-climatic system are described in Chapter 2. The three following chapters—published as peer-reviewed journal articles—address the specific research objectives and represent the main part of this thesis:

- Chapter 3 (Paper 1) describes the spatio-temporal snowmelt tracer variability and its impact on tracer-based hydrograph separation results. The event-based snowmelt component is quantified during the early and the peak snowmelt period in the Rofental and inferred runoff generation processes during the snow ablation period are described.
- Chapter 4 (Paper 2) deals with the ice melt component of streamflow which was analysed with tracer-based hydrograph separation for six events throughout a glacier ablation period in a subcatchment of the Rofental. The sensitivity of the estimated ice melt component to the water sampling strategy is quantified. Furthermore the rain and groundwater contribution to runoff generation is discussed.
- Chapter 5 (Paper 3) unravels the catchment transit time and the subsurface storage potential of the Rofental with a surface energy-balance/lumped parameter transit time model coupling approach. The process understanding developed in Chapter 3 and 4 supported the modelling approach which was conducted for a consecutive 4-year period.

Chapter 6 presents a perceptual model of how the Rofental catchment functions by describing the key hydrological processes that control the runoff and tracer response of the stream. This chapter connects the published work with respect to the overall research aim. Chapter 7 embeds the thesis outcome in a broader context and outlines the open questions, raising interesting and exciting opportunities for future research.
2 The high-elevation research catchment Rofental

Basic overview
The 98 km² high-elevation research catchment Rofental (Fig. 2-1a) is a valley that is remotely located in the Central Eastern Alps (Oetztal Alps) and mainly belongs to Austria (98 % of the catchment area) and partly to Italy (2 % of the catchment area). It is a headwater catchment of the Oetztaler Ache and the down flowing water finds its ultimate fate in the Black Sea. It is a near-natural catchment, with scarce human interference. Human interference includes a skiing area in Italy (‘Schnalstaler Gletscher’), extensive grazing by sheep and sustainable tourism (mountaineering huts). The highest permanent settlement of Austria, ‘Rofen’ (2011 m a.s.l.), is located at the entrance of the valley.

![Image](image_url)

Fig. 2-1: (a) Rofenache catchment and nested Hochjochbach catchment. (b) Red shape shows location of Rofenache catchment within Austria. (c) Hypsometric curve derived from 10 m digital elevation model.

The elevation ranges from 1889 m (a.s.l.) at the outlet of the catchment (gauging station at the village Vent, 46.8572° N, 10.9108° E) to 3768 m (a.s.l.), the highest peak of the Oetztal Alps (Wildspitze). A large fraction of the catchment area is located close to the mean elevation (flat slope of hypsometric curve in Fig. 2-1c). Almost the entire valley area belongs to the protected area of Natura 2000. The Rofental is intensively studied since 150 years, including glaciological and hydro-climatological recordings and investigations (Strasser et al., 2018). The valley is part of a research cooperation of three institutions: the Department of Geography at the University of Innsbruck (Austria); the Department of Atmospheric and Cryospheric Sciences...
at the University of Innsbruck (Austria); the Commission for Geodesy and Glaciology of the Bavarian Academy of Sciences (Germany). It is also a long-term ecological research (LTER) site and belongs to the long-term socio-ecological research (LTSER) platform ‘Tyrolean Alps’. Furthermore the well-instrumented catchment is also part of the International Network for Alpine Research Catchment Hydrology (INARCH) and the Euromediterranean Network of Experimental and Representative Basins (ERB). More detailed information of land cover, geology, glaciology, geomorphology and hydro-climatologic characteristics can be found in Strasser et al. (2018) and in Chapters 3 to 5.

Hydro-climatologic system description
The study area spans an elevation range of almost 2000 m which results in various climatic zones crossing the tree line and the snow line. The climate is classified as an ET and EF climate according to the Köppen-Geiger classification scheme. The ‘Latschbloder’ weather station (Fig. 2-1a), set up and operated by the University of Innsbruck since 2013, is closely located at mean catchment elevation and provides 5-year temperature and precipitation record from 2014 to 2018 (Fig. 2-2) which supports to understand the atmospheric conditions in the Rofental. The mean annual temperature is -2.3 °C and the mean monthly temperature ranges from -9.8 °C (February) to 6 °C (July). The mean annual precipitation sum during the period was 1125 mm and the mean monthly precipitation sums range from 53 mm (February) to 163 mm (August).

![Graph](image-url)

**Fig. 2-2:** (a) Mean monthly temperature and (b) mean monthly precipitation sum at Latschbloder (2919 m a.s.l.) during the period 2014 to 2018 based on measurements with a 10-minute interval. 15% and 7% of the data is missing for temperature and precipitation, respectively.
The river Rofenache (depicted in Fig. 2-1a) is mostly undisturbed by human interferences and has a typical glacial flow regime (Fig. 2-3a) following the seasonal cycle of temperature (Fig. 2-2). The mean annual runoff during the period 2014 to 2018 was 1454 mm per year. The range of mean monthly runoff during this period was 13 to 379 mm per month (i.e. the months February and July). Daily runoff ranges from 0.4 to 31.5 mm per day. A flow duration curve (FDC) depicts discharge against its exceedance probability for a time series and reveals the overall hydrologic response. In other words, it shows the relation of magnitude and frequency of streamflow discharges (Smakhtin, 2001). The FDC of the Rofenache for the period 2014 to 2018 can be seen in Fig. 2-3b. The 10th and 90th percentile flows are 12.5 and 0.5 mm per day (Fig. 2-3b). Median flow ($Q_{50}$) is 1.4 mm per day and the low slope of the low flow section (on the right side of $Q_{50}$) indicates sustainable subsurface contribution to streamflow (Smakhtin, 2001). The groundwater portion can be approximated by the $Q_{90}/Q_{50}$ ratio, i.e. 36 % (Nathan and McMahon, 1990).

Fig. 2-3: (a) Mean monthly runoff and runoff regime, as well as (b) flow duration curve of the period 2014 to 2018. Data basis is hourly measurements at Vent/Rofenache.
3 Paper 1: The importance of snowmelt spatiotemporal variability for isotope-based hydrograph separation in a high-elevation catchment

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My contribution to this article: study design, field work, laboratory work, run mixing model, producing plots, analysing results, and writing article.

Abstract
Seasonal snow cover is an important temporary water storage in high-elevation regions. Especially in remote areas, the available data is often insufficient to accurately quantify snowmelt contributions to streamflow. The limited knowledge about the spatio-temporal variability of the snowmelt isotopic composition, as well as pronounced spatial variation in snowmelt rates lead to high uncertainties in applying the isotope-based hydrograph separation method. The stable isotopic signatures of snowmelt water samples collected during two spring 2014 snowmelt events at a north- and a south-facing slope were volume-weighted with snowmelt rates derived from a distributed physics-based snow model in order to transfer the measured plot-scale isotopic composition of snowmelt to the catchment scale. The observed δ¹⁸O values and modelled snowmelt rates showed distinct inter- and intra-event variations, as well as marked differences between north- and south-facing slopes. Accounting for these differences, two-component isotopic hydrograph separation revealed snowmelt contributions to streamflow of 35±3 % and 75±14 % for the early and peak melt season, respectively. These values differed from those determined by formerly used weighting methods (e.g. using observed plot-scale melt rates) or considering either the north- or south-facing slope by up to 5 and 15 %, respectively.
3.1 Introduction

In many headwater catchments, seasonal water availability is strongly dependent on cryospheric processes and understanding these processes becomes even more relevant in a changing climate (APCC, 2014; IPCC, 2013; Weingartner and Aschwanden, 1992). The seasonal snow cover is an important temporary water storage in alpine regions. The timing and amount of water released from this storage is important to know for water resources management, especially in downstream regions where the water is needed (drinking water, snow making, hydropower, irrigation water) or where it represents a potential risk (flood, drought). Environmental tracers are a common tool to investigate the hydrological processes, but scientific studies are still rare for high-elevation regions because of the restricted access and high risk for field measurements in these challenging conditions.

Two-component isotope hydrograph separation (IHS) is a technique to separate streamflow into different time source components (event water, pre-event water) (Sklash et al., 1976). The event component depicts water that enters the catchment during an event (e.g. snowmelt) and is characterized by a distinct isotopic signature, whereas pre-event water is stored in the catchment prior to the onset of the event (i.e. groundwater and soil water which form baseflow) and is characterized by a different isotopic signature (Sklash and Farvolden, 1979; Sklash et al., 1976). The technique dates back to the late 1960s (Pinder and Jones, 1969) and was initially used for separating storm hydrographs in humid catchments. The first snowmelt-based studies were conducted in the 1970s by Dinçer et al. (1970) and Martinec et al. (1974). These studies showed a large pre-event water fraction (>50 %) of streamflow that changed the understanding of the processes in catchment hydrology fundamentally (Klaus and McDonnell, 2013; Sklash and Farvolden, 1979) and forced a paradigm shift, especially for humid temperate catchments. However, other snowmelt-based studies in permafrost or high-elevation catchments (Huth et al., 2004; Liu et al., 2004; Williams et al., 2009) revealed a large contribution of event water (>70 %), depending on the system state (e.g. frost layer thickness and snow depth), catchment characteristics and runoff generation mechanisms.

Klaus and McDonnell (2013) highlighted the need to quantify and account for the spatial variability of the isotope signal of event water, which is still a vast uncertainty in snowmelt-based IHS. In the literature inconclusive results prevail with respect to the variation of the isotopic signal of snowmelt. Spatial variability of snowmelt isotopic composition was statistically significant related to elevation (Beaulieu et al., 2012) in a catchment in British Columbia, Canada with 500 m relief. Moore (1989) and Laudon et al. (2007) found no statistical significant variation in their snowmelt $\delta^{18}$O data, due to the low gradient and small elevation range (approximately 30 m and 290 m) in their catchments, which favours an isotopically more homogenous snow cover. The effect of the aspect of the hillslopes on isotopic variability and IHS results in topographically complex terrain has been rarely investigated. Dahlke and Lyon (2013) and Dietermann and Weiler (2013) surveyed the snowpack isotopic composition and showed a notable spatial variability in their data, particularly between north- and south-facing slopes. They conclude that the spatial variability of snowmelt could be high and that the timing of meltwater varies with the morphology of the
catchment. Dietermann and Weiler (2013) also concluded that an elevation effect (decrease of snowpack isotopic signature with elevation), if observed, is disturbed by fractionation due to melt/refreeze processes during the ablation period. Aspect and slope are therefore important factors that affect the isotopic evolution of the snow cover and its melt (Cooper, 2006). In contrast, there have been various studies that have investigated the temporal variability of the snowmelt isotopic signal, e.g. by the use of snow lysimeters (Hooper and Shoemaker, 1986; Laudon et al., 2002; Liu et al., 2004; Maulé and Stein, 1990; Moore, 1989; Williams et al., 2009). During the ablation season the isotopic composition of the snowpack changes due to percolating rain and melt water and fractionation caused by melting, refreezing and sublimation (Dietermann and Weiler, 2013; Lee et al., 2010; Unnikrishna et al., 2002; Zhou et al., 2008), which leads to a homogenization of the isotopic profile of the snowpack (Árnason et al., 1973; Dinçer et al., 1970; Stichler, 1987) and an increase in heavy isotopes of meltwater throughout the freshet period (Laudon et al., 2007; Taylor et al., 2001; Taylor et al., 2002; Unnikrishna et al., 2002). Therefore, the characterization and the use of the evolving isotopic signal of snowmelt water instead of single snow cores is crucial for applying IHS (Taylor et al., 2001; 2002).

There have been various approaches to cope with the temporal variability of the input signal. If one uses more than one δ¹⁸O snowmelt sample for applying the IHS method, it is important to weight the values with appropriate melt rates, e.g. measured from the outflow of a snow lysimeter. Common weighting methods are the volume-weighted average approach (VWA), as used by Mast et al. (1995), and the current meltwater approach (CMW), applied by Hooper and Shoemaker (1986). Laudon et al. (2002) developed the runoff-corrected event water approach (runCE), which accounts for both, the temporal isotopic evolution and temporary storage of meltwater in the catchment and overcomes the shortcoming of the exclusion of residence times by VWA and CMW. This method was also deployed in several other snowmelt-based IHS (Beaulieu et al., 2012; Carey and Quinton, 2004; Laudon et al., 2004; Laudon et al., 2007).

Tracers have successfully been used in modelling studies to provide empirical insights into runoff generation processes and catchment functioning (Birkel and Soulsby, 2015; Birkel et al., 2011; Capell et al., 2012; Uhlenbrook and Leibundgut, 2002), but the combined use of distributed modelling and isotope tracers in snow-dominated environments is rare. Ahluwalia et al. (2013) used an isotope and modelling approach to derive snowmelt contributions to streamflow and determined differences between the two techniques of 2%. Distributed modelling can provide areal melt rates that can be used for weighting the measured isotopic composition of meltwater. Pomeroy et al. (2003) described the differences of insolation between north- and south-facing slopes in complex terrain that lead to spatial varying melt rates of the snowpack throughout the freshet period. The use of the areal snowmelt data from models will likely reduce the uncertainty that arises from the representativeness of measured melt rates at the plot-scale.

The overall goal of our study was to quantify the contribution of snowmelt to streamflow and hence to improve the knowledge of hydroclimatological processes in high-elevation catchments. This study aims to enhance the reliability of isotope-based hydrograph separation
by considering the distinct spatio-temporal variability of snowmelt and its isotopic signature in a high-elevation study region. This study has the following three objectives: 1) the estimation of the spatio-temporal variability of snowmelt and its isotopic composition, 2) the quantification of the impact of the spatial variability in snowmelt rates and its isotopic composition on isotope-based hydrograph separation (IHS) and 3) to assess the combined use of a physically-based snowmelt model and traditional IHS to determine snowmelt contributions to streamflow. Distributed melt rates provided by a surface energy balance model were used to weight the measured isotopic composition of snowmelt in order to characterize the event water isotopic composition. Traditional weighting methods (e.g. using plot-scale observed melt rates) were compared with the model approach.

3.2 Study area

The 98 km$^2$ high-elevation catchment of the Rofenache stream is located in the Central Eastern Alps (Oetztal Alps, Austria), close to the main Alpine ridge. The basin ranges in elevation from approximately 1900 m (a.s.l.) to 3770 m (a.s.l.). Average slope is 25° and average elevation is 2930 m (a.s.l.) (calculated from a 50 m digital elevation model). A narrow riparian zone (<100 m width) is located in the valley floor. The predominantly south- (SE) and north-facing (NNW) slopes form the main valley (cf. Fig. 3-1a), which trends roughly from southwest to northeast (cf. Fig. 3-1b). The study area has a dry inner-alpine climate. Mean annual precipitation is 800 mm yr$^{-1}$, of which 44 % falls as snow. The mean annual temperature at the gauging station in Vent (1890 m (a.s.l.), reference period: 1982-2003) is 2 °C. Seasonal snow cover typically lasts from October to the end of June at the highest regions of the valley.

The bedrock consists of mainly paragneiss and mica schist and is overlain by a mantle of glacial deposits and thin soils (<1 m). The bedrock outcrops and unconsolidated bare rocks cover the largest part (42 %) of the catchment (CLC, 2006). Glaciers cover approximately a third of the Rofenache catchment (35 %), while pastures and coniferous forests are located in the lowest parts of the catchment and cover less than 0.5 % (CLC, 2006). Sparsely vegetated areas and natural grassland cover 15 and 7.5 %, respectively (CLC, 2006). Besides seasonally frozen ground at slopes of various expositions, permafrost is likely to occur at an elevation over 2600 m (a.s.l.) at the north-facing slopes (Haeberli, 1975). The annual hydrograph reveals a highly seasonal flow regime. The mean annual discharge is 4.5 m$^3$ s$^{-1}$ (reference period: 1971-2009) and is dominated by snow and glacier melt during the ablation season, which typically lasts from May to September. The onset of the early snowmelt season in the lower part of the basin is typically in April.
3.3 Methods

3.3.1 Field sampling, measurements and laboratory analysis

The field work was conducted during the 2014 snowmelt season between the beginning of April and the end of June. Two short-term melt events (3 days) were investigated to illustrate the difference between early spring season melt and peak melt. The events were defined as warm and precipitation-free spells, with clear sky and dry antecedent conditions (i.e. no precipitation was observed 48 h prior to the event). Low discharge and air temperatures with a small diurnal variation and low melt rates, as well as a snow-covered area (SCA) of about 90% in the basin (Fig. 3-2a) characterize the conditions of the early melt event at the end of April (cf. Fig. 3-3b). In contrast, the peak melt period at the end of June is characterized by high discharge and melt rates, a flashy hydrograph, high air temperatures with remarkable diurnal variations (Fig. 3-3c) and a strongly retreated snowline (SCA: 66%; cf. Fig. 3-2c). Discharge data are available at an hourly resolution for the gauging station in Vent and meteorological data are obtained by 2 automatic weather stations (hourly resolution) located in and around the basin (Fig. 3-1).
The stream water sampling for stable isotope analysis consisted of pre-freshet baseflow samples at the beginning of March, sub-daily samples (temporal resolution ranges between 1 and 4 hours) during the two studied events and a post-event sample in July as indicated in Fig. 3-3a (grey-shaded area). Samples of snowmelt, snowpack and surface overland flow (if observed) were collected at the south- (S1, S2) and north-facing slope (N1, N2), as well as on a wind-exposed ridge (Fig. 3-1b) using a snowmelt collector. At each test site a snow pit was dug to install a 0.1 m$^2$ polyethylene snowmelt collector at the ground-snowpack interface. The snowmelt collector consists of a pipe that drains the percolating meltwater into a fixed plastic bag. Tests yield a preclusion of evaporation for this sampling method. Composite daily snowmelt water samples (bulk sample) were collected in these bags and transferred to polyethylene bottles in the field before the onset of the diurnal melt cycle. Furthermore, sub-daily grab melt samples were collected at S1 (on 23 April) and at N2 (on 07 June) to define the diurnal variability of the respective melt event. Unfortunately further sub-daily snowmelt sampling was not feasible. The pit face was covered with white styrofoam to protect it from direct sunlight. Stream, surface overland flow and grab snowmelt water samples were collected in 20 mL polyethylene bottles. Snow samples from snow pit layers were filled in airtight plastic bags and melted below room temperature before transferring them in bottles. Overall, 144 samples were taken during the study period. Snow water equivalent (SWE), snow height (HS), snow density (SD), and various snowpack observations (wetness and hand hardness index) were observed before the onset of the diurnal melt cycle at the study plots (Fig. 3-1). Mean SWE was determined by averaging five snow tube measurements within an area of 20 m$^2$ at each site. Daily melt rates were calculated by subtracting succeeding SWE values. Sublimation was neglected, as it contributes only to a small percentage (~10 %) to the seasonal water balance in high altitude catchments in the Alps (Strasser et al., 2008).
Fig. 3-3: (a) Daily precipitation, air temperature, and discharge at the outlet of the catchment during the complete study period; Hourly hydro-climatologic data of a 7-day period around the (b) early melt and (c) peak melt event. Grey-shaded areas indicate the investigated events.

All samples were treated by the guidelines proposed by Clark and Fritz (1997) and were stored dark and cold until analysis. The isotopic composition of the samples (δ18O, δD) was measured with cavity ring-down spectroscopy (Picarro L1102-i). Results are expressed in the delta notation as parts per thousand relative to the Vienna Standard Mean Ocean Water (VSMOW2). The mean laboratory precision (replication of 8 measurements) for all measured samples was 0.06 ‰ for δ18O. Due to the covariance of δ2H (δD) and δ18O (Fig. 3-5), all analyses were done with oxygen-18 values.

### 3.3.2 Model description

For the simulation of the daily melt rates, the non-calibrated, distributed, and physically-based hydroclimatological model AMUNDSEN (Strasser, 2008) was applied. Model features include interpolation of meteorological fields from point measurements (Marke, 2008; Strasser, 2008); simulation of short- and longwave radiation, including topographic and cloud effects (Corripio, 2003; Greuell et al., 1997); parameterization of snow albedo depending on snow age and temperature (Rohrer, 1991); modelling of forest snow and meteorological processes (Liston and Elder, 2006; Strasser et al., 2011); lateral redistribution of snow due to gravitational (Gruber, 2007) and wind-induced (Helfricht, 2014; Warscher et al., 2013) processes; and determination of snowmelt using an energy balance approach (Strasser, 2008). Besides having been applied for various other Alpine sites in the past (Hanzer et al., 2014; Marke et al., 2015; Pellicciotti et al., 2005; Strasser, 2008; Strasser et al., 2008; Strasser et al.,
AMUNDSEN has recently been set up and extensively validated for the Oetztal Alps region (Hanzer et al., 2016). This setup was also used to run the model in this study for the period 2013–2014 using a temporal resolution of 1 hour and a spatial resolution of 50 meters. In order to determine the model performance during the study period, catchment-scale snow distribution by satellite-derived binary snow cover maps and plot-scale observed SWE data were used for the validation (cf. Chapter 3.4.2). Therefore the spatial snow distribution as simulated by AMUNDSEN was compared with a set of MODIS (500 m spatial resolution) and Landsat (30 m resolution, subsequently resampled to the 50 m model resolution) snow maps with less than 10 % cloud coverage over the study area using the methodology described in Hanzer et al. (2016). Model results were evaluated using the performance measures BIAS, accuracy (ACC) and critical success index (CSI) (Zappa, 2008). ACC represents the fraction of correctly classified pixels (either snow-covered or snow-free both in the observation and the simulation). CSI describes the number of correctly predicted snow-covered pixels divided by the number of times where snow is predicted in the model and/or observed, and BIAS corresponds to the number of snow-covered pixels in the simulation divided by the respective number in the observation. ACC and CSI values range from 0 to 1 (where 1 is a perfect match), while for BIAS values below 1 indicate underestimations of the simulated snow cover, and values above 1 indicate overestimations. At the plot-scale, observed SWE values were compared with AMUNDSEN SWE values represented by the underlying pixel at the location of the snow course. Catchment-scale melt rates are calculated by subtracting two consecutive daily SWE grids, neglecting sublimation losses, as also done to achieve observed melt rates at the plot-scale. Subsequently, the DEM was used to calculate an aspect grid and further to divide the catchment into two parts: grid cells with aspects ranging from ≥270° to ≤90° were classified as ‘north-facing’, while the remaining cells were attributed to the class ‘south-facing’. Finally, these two grids were combined to derive melt rates for the south-facing (melt_s) and for the north-facing slope (melt_n).

3.3.3 Isotopic hydrograph separation, weighting approaches and uncertainty analysis

IHS is a steady-state tracer mass balance approach and several assumptions underlie this simple principle, which are described and reviewed in Buttle (1994) and Klaus and McDonnell (2013):

(1) The isotopic compositions of event and pre-event water are significantly different.
(2) The event water isotopic signature has no spatio-temporal variability, or variations can be accounted for.
(3) The pre-event water isotopic signature has no spatio-temporal variability, or variations can be accounted for.
(4) Contributions from the vadose zone must be negligible or soil water should be isotopically similar to groundwater.
(5) There is no or minimal discharge contribution from surface storage.
The focus of this study is on one of the assumptions: the spatio-temporal variability of event water isotopic signature is absent or can be accounted for. The fraction of event water \( f_e \) contributing to streamflow was calculated from Eq. 3-1.

\[
f_e = \frac{(C_p - C_s)}{(C_p - C_e)} \tag{3-1}
\]

The tracer concentration of the pre-event component \( C_p \) is the \( \delta^{18}O \) composition of baseflow prior to the onset of the freshet period, constituted mainly by groundwater and potentially by soil water which was assumed to have the same isotopic signal as groundwater. Tracer concentration \( C_e \) is the isotopic composition of stream water for each sampling time. The isotopic compositions of snowmelt samples were weighted differently to obtain the event water tracer concentration \( C_e \) using the following five weighting approaches:

1. volume-weighted with observed plot-scale melt rates (VWO)
2. equally weighted, assuming an equal melt rate on north- and south-facing slopes (VWE)
3. no weighting, only south-facing slopes considered (SOUTH)
4. no weighting, only north-facing slopes considered (NORTH)
5. volume-weighted with simulated catchment-scale melt rates (VWS)

Eq. 3-2 is the VWS approach with simulated melt rates for north- and south-facing slopes as described in Chapter 3.3.2, where \( M \) is the simulated melt rate (in mm d\(^{-1}\)), \( \delta^{18}O \) is the isotopic composition of sampled snowmelt and subscripts \( s \) and \( n \) indicate north and south, respectively. For obtaining the value of \( C_e \) a daily timestep \( (t) \) is used, considering daily melt rates and the isotopic composition of the daily bulk snowmelt samples.

\[
C_e(t) = \frac{M_s(t)\delta^{18}O_s(t) + M_n(t)\delta^{18}O_n(t)}{M_s(t) + M_n(t)} \tag{3-2}
\]

An uncertainty analysis (Eq. 3-3) was performed according to the Gaussian standard error method proposed by Genereux (1998):

\[
W_{te} = \left\{ \left[ \frac{C_p - C_s}{(C_p - C_e)^2} W_{C_e} \right]^2 + \left[ \frac{C_s - C_e}{(C_p - C_e)^2} W_{C_p} \right]^2 + \left[ \frac{-1}{(C_p - C_e)^2} W_{C_s} \right]^2 \right\}^{1/2} \tag{3-3}
\]

where \( W \) is the uncertainty, \( C \) is the isotopic composition, \( f \) is the fraction and the subscripts \( p, s \) and \( e \) refer to the pre-event, stream and event component. This assumes negligible errors in the discharge measurements and the melt rates (modelled and observed). The uncertainty of streamflow \( (W_{C_s}) \) is assumed to be equal to the laboratory precision (0.06 \( \% \)). For the uncertainty of the event component \( (W_{C_e}) \), the diurnal temporal variability (standard deviation) of the snowmelt isotopic signal (from one site and one day) was multiplied by the
appropriate value of the two-tailed t-table (dependent on sample number) and used for the event, as proposed by Genereux (1998). This resulted in different uncertainty values for the early melt event ($W_{ce} = 0.2 \%$) and the peak melt event ($W_{ce} = 0.5 \%$). An error of 0.04 \% was assumed for the pre-event component ($W_{cp}$), which reflects the standard deviation of two baseflow samples. A 95 \% confidence level was used. Spatial variation in snowmelt and its isotopic composition were not considered in this error calculation method as they represent the hydrologic signal of interest.

3.4 Results

3.4.1 Spatio-temporal variability of streamflow and stable isotopic signature of sampled of water sources

Two major snowmelt pulses (Mid-May and beginning of June) and four less pronounced ones between mid-March to early May occurred during the snowmelt season (Fig. 3-3a). Peak melt occurred at the beginning of June with maximum daily temperatures and runoff of 15 °C and 18 mm d$^{-1}$, respectively. The following high-flows were affected by rain (Fig. 3-3a) and glacier melt due to the strongly retreated snow line and snow-free ablation area of the glaciers in July.

Diurnal variations in discharge were strongly correlated with diurnal variations in air temperature (Fig. 3-3b and c) with a time lag of 3-5 hours for the early melt event and 2-3 hours for the peak melt event. An inverse relationship between streamflow $\delta^{18}$O and discharge was found for the early melt event (Fig. 3-4a and c). Small diurnal responses of streamflow $\delta^{18}$O were identified for both events, but were masked due to missing data during the recession of the hydrograph.

![Graph](https://via.placeholder.com/150)

Fig. 3-4: Linearly interpolated stream isotopic content of Rofenache for (a) the early melt and (b) the peak melt event. Dots indicate measurements. Event and pre-event
The importance of snowmelt spatiotemporal variability for isotope-based hydrograph separation in a high-elevation catchment

...water contributions during (c) the early melt and (d) the peak melt event calculated with the VWS approach.

The quality control of the isotopic data was performed by the $\delta^2\text{H}-\delta^{18}\text{O}$ plot (Fig. 3-5), which indicated no shift in the linear regression line and thus no secondary fractionation effects (evaporation) during storage and transport of the samples. The slope of the linear regression (slope=8.5, n=144, $R^2=0.93$) of the measurement data slightly deviates from that of the global meteoric (slope=8) and local meteoric water line (slope=8.1) based on monthly data from the ANIP (Austrian Network of Isotopes in Precipitation) sampling site in Obergurgl, which is located in an adjacent valley (reference period: 1991-2014). The small deviation (visible in Fig. 3-5) of the sampled water (i.e. snowpack and snowmelt) could indicate fractionation effects induced by phase transition (i.e. melt/refreeze and sublimation). The significant differences between the isotopic signatures of pre-event streamflow and snowmelt water enabled the IHS.

![Graph](image.png)

**Fig. 3-5: Relationship between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of water sources sampled during the snowmelt season 2014 in the Rofen valley, Austrian Alps.**

Overall, the $\delta^{18}\text{O}$ values ranged from -21.5 to -15.0‰, while snowpack samples were characterized by the most negative and pre-event baseflow samples by the least negative values. Snowpack samples showed a wide isotopic range, while streamflow samples revealed the narrowest spread, reflecting a composite isotopic signal mixing of the water components. Fig. 3-6 shows the $\delta^{18}\text{O}$ data of the water samples grouped into different categories and split into early and peak melt data. It shows the different $\delta^{18}\text{O}$ ranges and medians of the sampled water sources (Fig. 3-6a), as well as marked spatio-temporal variations in the isotopic signal.
(Fig. 3-6a and c). It is apparent that the snowpack δ¹⁸O values have a larger variation compared to the snowmelt data due to homogenization effects (Fig. 3-6a), as was also shown by Árnason et al. (1973), Dinçer et al. (1970) and Stichler (1987). The median of the δ¹⁸O of snowmelt was higher than that of the snowpack indicating fractionation. The median δ¹⁸O of surface overland flow was higher than that of snowmelt (Fig. 3-6a) for the early and peak melt period. Overall, the peak melt δ¹⁸O values (Fig. 3-6b) were less variable and had a higher median than the early melt values, because fractionation effects (due to melt/refreeze and sublimation) most likely altered the isotopic composition of the snowpack over time (cf. Taylor et al., 2001, 2002). One major finding was that the δ¹⁸O values on the north-facing slope had a larger range and a lower median compared to the opposing slope (Fig. 3-6c). Samples from the wind drift influenced site (also south-exposed) were more depleted in heavy isotopes compared to the south-facing slope samples (Fig. 3-6c).

Fig. 3-6: Jittered dot plots for δ¹⁸O of collected water samples split into (a) water sources, (b) stage of snowmelt and (c) spatial origin. Grey circles indicate early melt samples and black circles peak melt samples. The grey and black line represents the median of early and peak melt data, respectively. nₑ is the number of early melt samples and nₚ is the number of peak melt samples.

In general, the average snowmelt and snowpack isotopic composition was more depleted for the early melt period (Tab. 3-1) and changed over time because fractionation likely altered the snowpack and its melt. It is obvious that the isotopic evolution (gradually enrichment) on the south-facing slope took place earlier in the annual melting cycle of the snow, and indicates a premature snowpack concerning the enrichment of isotopes and earlier ripening compared to the north-facing slope.
Tab. 3-1: Average isotopic composition of snowpack and snowmelt with standard deviation for north- and south-facing slopes during the early and the peak melt event. Values are averages of three consecutive days.

<table>
<thead>
<tr>
<th></th>
<th>North-facing slope</th>
<th>South-facing slope</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Snowpack δ¹⁸O (%)</td>
<td>Snowmelt δ¹⁸O (%)</td>
</tr>
<tr>
<td>Early melt event</td>
<td>-19.7±0.6 (n=12)</td>
<td>-18.8±0.2 (n=3)</td>
</tr>
<tr>
<td>Peak melt event</td>
<td>-17.6±0.4 (n=18)</td>
<td>-17.9±0.1 (n=3)</td>
</tr>
</tbody>
</table>

Tab. 3-1 shows that meltwater sampling throughout the entire snowmelt period is required to account for the temporal variation in the isotopic composition of the snowpack (cf. Taylor et al., 2001, 2002). In detail, the snowpack and snowmelt δ¹⁸O data highlighted a marked spatial inhomogeneity between north- and south-facing slopes throughout the study period. The snowpack isotopic composition from both sampled slopes was statistically different for the early melt, but not for the peak melt (with Kruskal-Wallis test at 0.05 significance level), whereas the snowmelt δ¹⁸O showed a significant difference throughout the study period (Fig. 3-7).

Sub-daily snowmelt samples (n=5) at S1 (23 April 2014) had a range of 0.1 ‰ in δ¹⁸O, and the bulk sample (integrating the entire diurnal melt cycle) was within the scatter of those values (Fig. 3-8). The intra-daily variability of snowmelt (n=3) at N2 (07 June 2014) was relatively higher with values ranging from -17.9 to -18.1 ‰. The bulk sample (-17.9 ‰) was at the upper end of those values (Fig. 3-8).
Stream water isotopic composition was more enriched in heavy isotopes during the early melt period and successively became more depleted throughout the freshet period, resulting in more negative values during peak melt (Tab. 3-2). The standard deviation and range of stream water δ¹⁸O during early melt was higher and could be related to an increasing snowmelt contribution throughout the event and larger diurnal amplitudes of snowmelt contribution compared to peak melt (Tab. 3-2).

**Tab. 3-2:** Descriptive statistics of streamflow isotopic composition at the outlet of the Rofenache during events of the snowmelt season 2014.

<table>
<thead>
<tr>
<th></th>
<th>Pre-event</th>
<th>Early melt</th>
<th>Peak melt</th>
<th>Post-event</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
<td>07/03</td>
<td>23/04 – 25/04</td>
<td>07/06 – 09/06</td>
<td>11/07</td>
</tr>
<tr>
<td>Average (δ¹⁸O ‰)</td>
<td>-15.02</td>
<td>-15.97</td>
<td>-16.87</td>
<td>-15.09</td>
</tr>
<tr>
<td>Standard deviation (δ¹⁸O ‰)</td>
<td>0.04</td>
<td>0.16</td>
<td>0.05</td>
<td>n/a</td>
</tr>
<tr>
<td>Range (δ¹⁸O ‰)</td>
<td>0.05</td>
<td>0.50</td>
<td>0.20</td>
<td>n/a</td>
</tr>
<tr>
<td>Number of samples</td>
<td>2</td>
<td>17</td>
<td>30</td>
<td>1</td>
</tr>
</tbody>
</table>

**3.4.2 Snow model validation and snowmelt variability**

Fig. 3-9 shows the values for the selected performance measures based on the available MODIS and Landsat scenes during the period March–July 2014. The results indicate a reasonable model performance with a tendency to slightly overestimate the snow cover during the peak melt season (BIAS >1). In general the CSI does not drop below 0.7 and 80 % of the pixels are correctly classified (ACC) throughout the study period. Fig. 3-2 shows the observed and simulated spatial snow distribution around the time of the two events. Despite a higher SCA during the early melt season (Fig. 3-2a and b) compared to the peak melt season (Fig. 3-2c and d) one can see the overestimation of the simulated SCA compared to the observed
Tab. 3-3: Comparison of observed and simulated (represented by the underlying pixel) SWE values.

<table>
<thead>
<tr>
<th>Site</th>
<th>Date</th>
<th>Stage of snowmelt season</th>
<th>SWE [mm]</th>
<th>Difference between observed and simulated SWE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Observed</td>
<td>Simulated</td>
</tr>
<tr>
<td>S1</td>
<td>2014-04-23</td>
<td>Early melt</td>
<td>141</td>
<td>151</td>
</tr>
<tr>
<td>N1</td>
<td>2014-04-23</td>
<td>Early melt</td>
<td>351</td>
<td>356</td>
</tr>
<tr>
<td>Wind</td>
<td>2014-04-24</td>
<td>Early melt</td>
<td>201</td>
<td>229</td>
</tr>
<tr>
<td>S1</td>
<td>2014-04-25</td>
<td>Early melt</td>
<td>113</td>
<td>78</td>
</tr>
<tr>
<td>N1</td>
<td>2014-04-25</td>
<td>Early melt</td>
<td>270</td>
<td>293</td>
</tr>
<tr>
<td>N2</td>
<td>2014-06-07</td>
<td>Peak melt</td>
<td>594</td>
<td>477</td>
</tr>
<tr>
<td>N2</td>
<td>2014-06-08</td>
<td>Peak melt</td>
<td>568</td>
<td>435</td>
</tr>
<tr>
<td>N2</td>
<td>2014-06-09</td>
<td>Peak melt</td>
<td>537</td>
<td>390</td>
</tr>
</tbody>
</table>

Mean deviation between observed and simulated SWE: 13%

Snowmelt (observed and simulated daily losses of SWE) showed a distinct spatial variation between the north-facing and the south-facing slope for the early melt (23/24 April), but less marked variations for the peak melt (07/08 June) period (Fig. 3-10). Relative day-to-day differences are more pronounced for the early melt season. Both simulated and observed melt rates are higher for the peak melt event on the south-facing slope, but not for the north-facing slope. Simulated melt intensity on the south-facing slope at the end of April was twice the rate on the north-facing slope, while simulated melt rates were approximately the same for the opposing slopes during peak melt. Simulated (catchment scale) snowmelt rates were markedly higher during the early melt (23 and 24 April) on the north-facing slope compared to the observed (plot scale) melt rates (Fig. 3-10a), but differences between them were small during peak melt for both slopes (07 and 08 June; Fig. 3-10).
3.4.3 Weighting techniques and isotope-based hydrograph separation

Differences between the applied snowmelt weighting techniques, induced by the high spatial variability of snowmelt (Chapter 3.4.2), led to different event water isotopic compositions ($C_e$) for the IHS analyses (Tab. 3-4). The event water component was depleted in $\delta^{18}O$ by roughly 0.3‰ for the second day (24 April) of the early melt event compared to the preceding day, but inter-daily variation during the peak melt is almost absent. Especially during early melt (23/04 to 24/04) strong deviations between observed plot-scale melt rates and distributed (areal) melt rates obtained by AMUNDSEN occurred (Fig. 3-11), and led to more different event water isotopic compositions between the VWS and the VWO approach (Tab. 3-4).

<table>
<thead>
<tr>
<th>Event water isotopic composition ($\delta^{18}O$ ‰)</th>
<th>23/04</th>
<th>24/04</th>
<th>07/06</th>
<th>08/06</th>
</tr>
</thead>
<tbody>
<tr>
<td>VWS</td>
<td>-17.9</td>
<td>-18.2</td>
<td>-17.5</td>
<td>-17.5</td>
</tr>
<tr>
<td>VWO</td>
<td>-18.3</td>
<td>-18.6</td>
<td>-17.4</td>
<td>-17.5</td>
</tr>
<tr>
<td>VWE</td>
<td>-18.1</td>
<td>-18.3</td>
<td>-17.5</td>
<td>-17.5</td>
</tr>
<tr>
<td>NORTH</td>
<td>-18.6</td>
<td>-18.8</td>
<td>-17.9</td>
<td>-17.9</td>
</tr>
<tr>
<td>SOUTH</td>
<td>-17.6</td>
<td>-17.9</td>
<td>-17.1</td>
<td>-17.1</td>
</tr>
</tbody>
</table>

The hydrograph and the results of the IHS applied with the VWS method for the early and peak melt event are presented in Fig. 3-4 and highlight the lower flow rates and higher pre-event fractions during early melt (Fig. 3-4c) and vice versa for the peak melt period (Fig. 3-4d).
The total runoff volume during the peak melt period was approximately six times higher than in the early melt period. The fractions of snowmelt (volume) estimated with the VWS approach were 35 and 75 % with calculated uncertainties (95 % confidence level) of ±3 and ±14 % for the early and peak melt event, respectively. The uncertainty calculated from Eq. 3-3 of the IHS applied with the VWS method was higher (14 %) for the peak melt event than for the early melt event because the difference between isotopic composition of pre-event water and event water was smaller than for the early melt event (uncertainty: 3 %) (cf. Tab. 3-2 and Tab. 3-4).

Throughout the early melt event, the snowmelt fraction increased from 25 to 44 % (Fig. 3-4c; Tab. 3-5). This trend mirrors the stream isotopic composition, which became more depleted (Fig. 3-4a). Event water contributions during peak melt were generally higher but had a smaller range (70 to 78 %; Fig. 4d). Diurnal isotopic variations of stream water were small for both events (Fig. 3-4a and b), and could not clearly be obtained due to missing data on the falling limb of the hydrographs.

<table>
<thead>
<tr>
<th>Event</th>
<th>Early Melt</th>
<th>Peak Melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
<td>23/04 - 25/04</td>
<td>07/06 - 09/06</td>
</tr>
<tr>
<td>Mean discharge</td>
<td>1.5 m³ s⁻¹</td>
<td>11.5 m³ s⁻¹</td>
</tr>
<tr>
<td>Peak discharge</td>
<td>1.9 m³ s⁻¹</td>
<td>17.4 m³ s⁻¹</td>
</tr>
<tr>
<td>Volume runoff</td>
<td>3.3 mm</td>
<td>20.7 mm</td>
</tr>
<tr>
<td>Mean event water fraction</td>
<td>35±3 %</td>
<td>75±14 %</td>
</tr>
<tr>
<td>Peak event water fraction</td>
<td>44±4 %</td>
<td>78±15 %</td>
</tr>
</tbody>
</table>
The use of the different weighting approaches led to strongly varying estimated snowmelt fractions of streamflow (Fig. 3-12). Especially the differences between the SOUTH and the NORTH approach during both investigated events (up to 24 %), and the differences between the VWS and the VWO approach (5 %) during early melt (Fig. 3-12a) are notable. Event water contributions estimated by the different weighting methods ranged from 21-28 % at the beginning of the early melt event up to 31-55 % at the end of the event (cf. Fig. 3-12a, Tab. 3-6). Minimum event water contributions during the peak melt were estimated at 60-84 % and maxima ranged between 67-94 % for the different weighting methods (Table 6, Fig. 3-12b). Beside these intra-event variations in snowmelt contribution, the volumetric variations at the event-scale were smaller and ranged between 28 to 40 % and 66 to 90 %, for the early and peak melt event, respectively (Tab. 3-6).

Considering only spatial variation of snowmelt isotopic signatures (i.e. comparing the NORTH/SOUTH approach with the VWE approach) for IHS led to differences in estimated event water fractions up to 7 and 14 % for the early and peak melt period, respectively (Tab. 3-6). However, considering only spatial variation in snowmelt rates (i.e. comparing the VWS/VWO approach with the VWE approach) led to differences in event water fraction up to 3 and 2 % for the early and peak melt period, respectively (Tab. 3-6).
Tab. 3-6: Event water contribution to streamflow based on the different weighting techniques. The error indicates the variability (standard deviation) and the values in parentheses depict the range.

<table>
<thead>
<tr>
<th>Event water contribution (%)</th>
<th>VWS</th>
<th>VWO</th>
<th>VWE</th>
<th>NORTH</th>
<th>SOUTH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early melt event</td>
<td>35±6</td>
<td>30±4</td>
<td>33±5</td>
<td>28±3</td>
<td>40±9</td>
</tr>
<tr>
<td>Peak melt event</td>
<td>75±2</td>
<td>78±3</td>
<td>76±2</td>
<td>66±2</td>
<td>90±3</td>
</tr>
<tr>
<td>(70-78)</td>
<td>(71-82)</td>
<td>(70-78)</td>
<td>(60-67)</td>
<td>(84-94)</td>
<td></td>
</tr>
</tbody>
</table>

Surface overland flow was not considered in the IHS analyses, but if applied, it would most likely increase the calculated snowmelt fraction slightly. Furthermore, snowmelt samples from the wind-exposed site were not used in the IHS analyses because this site was only sampled on the south-facing slope during early melt and is not representative for the catchment due to its limited coverage. However, incorporation of this data would decrease the calculated snowmelt fraction by approximately 2%.

### 3.5 Discussion

#### 3.5.1 Temporal variation in streamflow during the melting season

Snowmelt is a major contributor to streamflow during the spring freshet period in alpine regions and large amounts of snowmelt water infiltrate into the soil and recharge groundwater (Penna et al., 2014). The hydrological response of the stream followed the variations of air temperature, as already observed by Braithwaite and Olesen (1989) (Fig. 3-3a). The observed time lags (Fig. 3-3b and c) between maximum daily air temperature and daily peak flow are common in mountain catchments (Engel et al., 2016; Schuler, 2002). During peak melt, the flashy hydrograph revealed less variation in the timing of peak discharge of 7 day data (cf. Fig. 3-3c) compared to the early melt, as reported by Lundquist and Cayan (2002). The increase in discharge coincides with decreasing streamflow \(^{18}\)O during the early melt event (Fig. 3-4a and c) and confirms earlier findings of Engel et al. (2016) who identified inverse relationships between streamflow \(^{18}\)O and discharge during several 24-hour events in an adjacent valley on the southern side of the main Alpine ridge, although their findings rely on streamflow contributions from snow and glacier melt. The lower stream water isotopic composition during peak melt suggests a remarkable contribution of more depleted snowmelt to streamflow and therefore confirms the results of the IHS.

#### 3.5.2 Spatio-temporal variability of snowmelt and its isotopic signature

The rate of snowmelt varies spatially in catchments with complex topography (Carey and Quinton, 2004; Dahlke and Lyon, 2013; Pomeroy et al., 2003). This was also demonstrated for the Rofen valley in this study (Fig. 3-10, Tab. 3-3). Snowmelt results from a series of processes (e.g. energy exchange snow-atmosphere) that are spatially variable - especially in complex terrain. This also becomes obvious when comparing the snowmelt rates on 23 April 2014 in Fig. 3-10a. Differences of observed and simulated snowmelt rates might result from the non-
representativeness of point measurements for catchment averages and refer to the scale issue of data collection. The peak melt period was characterised by less spatial and day-to-day variation in observed melt rates (Fig. 3-10). The modelled daily snowmelt during this period was similar for north- and south-facing slopes, likely because of higher melt rates but also a smaller snow-covered area of the south-facing slope in contrast to the north-facing slope during peak melt (Fig. 3-11). The model performance was good for SWE (Tab. 3-3) and snow cover extent (Fig. 3-2 and Fig. 3-9). The spatial variation of snowpack isotopic composition are significant, as can be seen in the differences for north- and south-facing slopes, and also shown by Carey and Quinton (2004), Dahlke and Lyon (2013) and Dietermann and Weiler (2013) in their high-gradient catchments, whereas there are unclear differences for the spatial variation of the snowmelt isotopic signal in the literature. It is not clear to which extent altitude is important, as Dietermann and Weiler (2013) stated that a potential elevation effect (decrease in snowmelt $\delta^{18}O$ with elevation) is likely to be disturbed by melting processes (isotopic enrichment) depending on catchment morphology (aspect, slope) during the ablation period. Beaulieu et al. (2012) detected elevation as a predictor, which explained most of the variance they observed in snowmelt $\delta^{18}O$ from four distributed snow lysimeters. Moore (1989) and Laudon et al. (2007) found no significant difference of $\delta^{18}O$ in their lysimeter outflows, likely due to the small elevation gradient of their catchments which favours an isotopically homogenous snowpack, whereas Unnikrishna et al. (2002) found a remarkable small-scale spatial variability. An altitudinal gradient was not considered in this study, but possible effects on IHS are discussed in Chapter 3.5.6. The difference of snowmelt (not snowpack) isotopic signature between north- and south-facing slopes was clearly shown in this study. The dataset is small, but reveals clear differences induced by varying magnitudes and timing of melt due to differences in solar radiation on the opposing slopes (cf. Fig. 3-7). Temporal variability in snowmelt isotopic composition is greater for the north-facing slope compared to the south-facing slope (Fig. 3-7), which was also pointed out by Carey and Quinton (2004) in their subarctic catchment. Earlier homogenization in the isotopic profile of the snowpack and earlier melt out are responsible for this phenomenon (cf. Dincer et al., 1970; Unnikrishna et al., 2002). Fractionation processes likely controlled this homogenization of the snowpack between the two investigated melt events. The isotopic homogenization of the snowpack on the south-facing slope started earlier in the melting period and caused a smaller spatial and temporal variation compared to the north-facing snowpack, as also reported by Unnikrishna et al. (2002) and Dincer et al. (1970). The differences between these investigated snowpacks were larger in the early melt season than in the peak melt season. This affects the IHS results, especially because the snowmelt contributions from the south- and north-facing slope - with marked isotopic differences - were distinct. Due to melt, fractionation processes proceeded and the snowpack likely became more homogenous throughout the snowmelt season. However, inter-daily variations of snowpack isotopic composition, especially for the north-facing slope, were still observable during the peak melt period. The gradual isotopic enrichment of the snowpack was also observed for snowmelt, as described by many others (Feng et al., 2002; Shanley et al., 2002; Taylor et al., 2001; Taylor et al., 2002; Unnikrishna et al., 2002).
Intra-daily variations of snowmelt $\delta^{18}O$ could be quantified for two sites (Fig. 3-8). At S1 on the south-facing slope during the early melt event, the 0.1‰ range in $\delta^{18}O$ (n=5) was smaller than the range at N2 on the north-facing slope during the peak melt event (n=3, range=0.2‰). This sub-daily variability is markedly smaller than the differences between the investigated slopes (cf. Tab. 3-1), which ranged from 0.8‰ (peak melt) to 1.4‰ (early melt). Unnikrishna et al. (2002) described significant temporal variations of snowmelt $\delta^{18}O$ during large snowmelt events (peak melt). However, these findings could not be confirmed within this study, probably due to the temporally limited data and should be tested with a larger dataset. The bulk sample at S1 (23 April 2014) was isotopically closer to the sub-daily values compared to the bulk sample at N2 (07 June 2014) that was at the upper range of the sub-daily samples (Fig. 3-8). Therefore one could argue that for the south-facing slope there is a negligible uncertainty if one uses a single snowmelt value (at one time) for IHS instead of using a bulk sample, but this is not the case for the north-facing slope (cf. Fig. 3-8, site N2). Unfortunately the sample numbers are small, because more frequent and more distributed sampling (at different sites) was not feasible due to logistical issues. Hence these results should be used with caution and should be investigated in further studies. If the focus and the scale of the study is not on the sub-daily variability, the authors recommend to use bulk samples, because these integrate (automatically weighed with snowmelt rate) the diurnal variations.

### 3.5.3 Validity of isotopic hydrograph separation

The validity of IHS relies on several assumptions (cf. Chapter 3.3; Buttle, 1994; Klaus and McDonnell, 2013). The assumption that the isotopic composition of event and pre-event water differ significantly (Assumption 1) was successfully proven, because the snowmelt isotopic values were markedly lower than pre-event baseflow values (cf. Tab. 3-2 and Tab. 3-4, Fig. 3-5). Spatio-temporal variations of event water isotopic composition (Assumption 2) were accounted for by collecting daily and sub-daily samples during both events throughout the freshet period and meltwater sampling at a north- and south-facing slope, respectively. The spatially variable input of event water was considered by dividing the catchment into two parts – a north- and a south-facing slope. This study supports the findings of Dahlke and Lyon (2013) and Carey and Quinton (2004), emphasizing the highly variable snowpack/snowmelt isotopic composition in complex topography catchments due to enrichment. The temporal variability of event water isotopic composition was considered by using bulk daily samples, which integrate snowmelt from the entire diurnal melting cycle, but smooth out a sub-daily signal. Because the focus of this study was more on the inter-event than the intra-daily scale, this approach seemed reasonably reliable. The spatio-temporal variability of the isotopic composition of pre-event water (Assumption 3) is a major limitation and could not be clearly identified due to a lack of data and was therefore assumed to be constant. Small differences between the pre-event samples (-15.00‰ and -15.05‰ for $\delta^{18}O$) and post-event stream water isotopic composition support this assumption (Table 2). The assumption of soil water having the same isotopic composition as groundwater in time and space (Assumption 4) is critical. Some studies reveal no significant differences (e.g. Laudon et al., 2007), whereas others do (e.g. Sklash and Farvolden 1979). Isotopic differences between groundwater and soil water were not considered due to a lack of data. Furthermore, it is not
known to which degree the vadose zone contributes to baseflow in the study area. Winter baseflow used in the analyses is assumed to integrate mainly groundwater and partly soil water. Soil water could be hypothesized to have a negligible contribution to baseflow during winter due to the recession of the soil water flow in autumn and frozen soils in winter. The assumption that no or minimal surface storage occurs (Assumption 5) is plausible because water bodies like lakes or wetlands do not exist in the study catchment and due to the steep topography detention storage is likely limited. The transit time of snowmelt was assumed to be less than 24 h. This short travel time is characteristic for headwater catchments (Lundquist et al., 2005) with high in-channel flow velocities, steep hillslopes, a high drainage density with snow-fed tributaries, thin soils, most snowmelt originating from the edge of the snow-line (small average travel distances), partly frozen soil, and observed surface overland flow. The state-of-the-art method (runCE) to include residence times of snowmelt in the event water reservoir proposed by Laudon et al. (2002) was applied in several IHS studies (Beaulieu et al., 2012; Carey and Quinton, 2004; Petrone et al., 2007), but was not feasible due to the short-term character and temporally limited data.

3.5.4 Hydrograph separation results and inferred runoff generation processes

Large contributions from snowmelt to streamflow are common in high-elevation catchments. Daily contributions between 35 and 75 % in the Rofen valley are comparable to the results of studies conducted in other mountainous regions, mostly outside the European Alps. Beaulieu et al. (2012) estimated snowmelt contributions ranging from 7 to 66 % at the seasonal scale for their 2.4 km² catchment and reported contributions of 34 and 62 %, for the early melt and peak melt, respectively. The hydrograph was dominated by pre-event water during early melt in April (Fig. 3-4c), which is in accordance with the results obtained by other IHS studies (Beaulieu et al., 2012; Laudon et al., 2004; Laudon et al., 2007; Moore, 1989). The snowmelt contribution increased as the freshet period progressed and peaked with high contributions at the beginning of June. Beaulieu et al. (2012) and Sueker et al. (2000) reported comparable results for their physically similar catchments during peak melt with 62 and up to 76 % event water contributions to streamflow, respectively. At the event-scale comparable studies are rare. Engel et al. (2016) report a maximum daily snowmelt contribution estimated with a three-component hydrograph separation of 33 % for an 11 km² catchment southwest of the Rofen valley with similar physiographic characteristics, but on the southern side of the main Alpine ridge. It should be mentioned that in their study, runoff was fed by three components (snowmelt, glacier melt and groundwater) and lower snowmelt contributions were prevalent because most of the catchment area (69 %) was snow-free.

Initial snowmelt events flush the pre-event water reservoir as snowmelt infiltrates into the soil and causes the pre-event water to exfiltrate and contribute to the streamflow. As the soil and groundwater reservoir becomes gradually filled with new water (snowmelt), the event water fraction in the stream increases. The system is also wetter during peak melt. The dominance of event water in the hydrograph is interpreted as an outflow of pre-event water stored in the subsurface and the gradual replenishment of the soil and groundwater reservoirs by event...
3.5.5 Impact of spatial varying snowmelt and its isotopic composition on isotope-based hydrograph separation and assessment of weighting approaches

Klaus and McDonnell (2013) stress in their review paper the need to investigate the effects of the spatially varying snowmelt and its isotopic composition on IHS. This study quantified the impact of the spatially varying isotopic composition of snowmelt between north- and south facing slopes on IHS results for the first time. The IHS results were more sensitive to the spatial variability of snowmelt $\delta^{18}O$ than to spatial variations of snowmelt rates (Tab. 3-6). This is even more pronounced for the peak melt period, because snowmelt rates were similar for the north- and south-facing slope, probably due to a ripe snow cover throughout the catchment. The difference in volumetric snowmelt contribution to streamflow at the event-scale determined using the five different weighting methods for IHS is maximal 24 % (NORTH approach vs. SOUTH approach). The data show that the variations between the weighting approaches (VWS, VWO and VWE) are higher throughout the early melt season (Tab. 3-6), because small-scale variability of snowmelt and its isotopic composition are more pronounced in the early melt season. Thus the influence of spatial variability of snowmelt and its isotopic composition on the event water fraction calculated with IHS is larger during this time. Melt rates strongly differ between the south- and the north-facing slope (Fig. 3-11), which was deceptively gathered by manually measured SWE, likely due to micro-topographic effects. As the contributions from both slopes are used in Eq. 3-3, they strongly influence the average isotopic composition of event water. The weighting method SOUTH (or NORTH) represents the hypothetical and most extreme scenario in which only one sampling site is used for the IHS analysis. Because snowmelt is more depleted in $\delta^{18}O$ and closer to pre-event water isotopic composition on the south-facing slope during peak melt, this scenario has the greatest effect on IHS and leads to the strongest deviation in estimated snowmelt fractions (up to 15 % overestimation compared to the VWS approach). These scenarios (NORTH/SOUTH) are theoretical and it is obvious that it is not recommended to conduct a IHS analysis by using only samples from either north- or south-facing slopes in catchments with complex terrain. Similar to the VWE method, snowmelt isotopic data was not volume-weighted in other studies (e.g. Engel et al., 2016) where snowmelt data was not available. This has a more
distinct effect on IHS during the early melt season because of the higher spatio-temporal variability in snowmelt (and its isotopic composition) compared to the peak melt season and led to a deviation in the snowmelt fraction in streamflow of 2% and 3% compared to the VWS and VWO approach, respectively. These differences are small, because the differing snowmelt and isotopic values offset each other in this particular case (Tab. 3-6). Nevertheless the results of VWS are more correct for the right reason, because single observed plot-scale melt rates do not represent distributed snowmelt contribution at the catchment-scale. Therefore, one can hypothesize that distributed simulated melt rates enhance the reliability of IHS, whereas plot-scale weighting introduces a large error caused by the difficulty in finding locations that represent the average melt rate in complex terrain.

3.5.6 Limitations of the study
Collecting water samples in high-elevation terrain is challenging due to limited access and high risk (e.g. avalanches), limiting high-frequency sampling. Hence some limitations are inherent in this study. Potential elevation effects on snowmelt isotopic composition were not tested. The opposing sampling sites (S1-N1 and S2-N2) were at the same elevation (Fig. 3-1). It was assumed that the differences in north- and south-facing slopes were much greater than a possible altitudinal gradient in snowmelt isotopic composition. This hypothesis was not tested, but based on the results of other studies (Dietermann and Weiler, 2013). However, accounting for a potential altitudinal gradient (decrease in snowmelt $\delta^{18}O$ with elevation) would lead to more depleted isotopic signatures of event water and hence to lower event water fractions. Another disadvantage is that no snow survey was conducted prior to the onset of snowmelt (peak accumulation) to estimate spatial variability in bulk snow $\delta^{18}O$. Because snowmelt is used for applying IHS, it is not clear to which degree the spatial variability of the snowpack isotopic composition is important. Two-component isotopic hydrograph separation was successfully applied using the end-members snowmelt and baseflow, but potential contributions of glacier melt were neglected (here defined as ice/firn melt). Because glaciers in the catchment were still covered by snow during the peak melt season, a significant contribution from ice/firn melt was assumed to be unlikely. Nevertheless negligible amounts of basal (ice) meltwater could originate from temperate glaciers. No samples could be collected during the recession of the hydrograph (at night). Even though the spatial variability of the event water signal was the focus of the study, only temporal variability was considered in the Genereux-based uncertainty analyses. Although the temporal variability of winter baseflow isotopic composition seems to be insignificant, the sample number (n=2) could be too small to characterize the pre-event component and should be clearly investigated in future work. Penna et al. (2016) used two approaches to determine the isotopic composition of pre-event water and described differences in the estimated event water contributions during snowmelt events. They advise to take pre-event samples prior to the onset of the melt season because pre-event samples taken prior to the onset of the diurnal melt cycle could be affected by snowmelt water from the previous melt pulses and therefore to underestimated snowmelt fractions and high uncertainties. Furthermore, model results and observed discharges were assumed to be free of error in the analyses. As pointed out, instrumentation and accessibility
are major problems for high-elevation studies. For this study it turned out that composite snowmelt samples were easier to collect, representing the day-integrated melt signal. A denser network of melt collectors would be desirable, as well as a snow lysimeter to gain high-frequency data automatically. Representative samples of the elevation zones and different vegetation belts could be important too, especially in partly forested catchments with a distinct relief (cf. Unnikrishna et al., 2002).

3.6 Conclusions

This study provides new insights into the variability of the isotopic composition in snowmelt and highlights its impact on IHS results in a high-elevation environment. The spatial variability in snowmelt isotopic signature was considered by experimental investigations on south- and north-facing slopes to define the isotopic composition of the snowmelt end-member with greater accuracy. This study clearly shows that distributed snowmelt rates obtained from a model based on meteorological data from local automatic weather stations, affect the weighting of the event water isotopic signal, and hence the estimation of the snowmelt fraction in the stream by IHS. The study provides a variety of relevant findings that are important for hydrologic research in high-alpine environments. There was a distinct spatial variability in snowmelt between north- and south-facing slopes, especially during the early melt season. The isotopic composition of snowmelt water was significantly different between north-facing and south-facing slopes, which resulted in a pronounced effect on the estimated snowmelt contributions to streamflow with IHS. The IHS results were more sensitive to the spatial variability of snowmelt $\delta^{18}$O than to spatial variation of snowmelt rates. The differences in the estimated snowmelt fraction due to the weighting methods used for IHS were as large as 24%. This study also shows that it is hardly possible to characterize the event water signature of larger slopes based on plot-scale snowmelt measurements. Applying a distributed model reduced the uncertainty of the spatial snowmelt variability inherent to point-scale observations. Hence, applying the VWS method provided more reasonable results than the VWO method. This study highlighted that the selection of sampling sites has a major effect on IHS results. Sampling at least north-facing and south-facing slopes in complex terrain and using distributed melt rates to weight the snowmelt isotopic composition of the differing exposures is therefore highly recommended for applying snowmelt-based IHS.

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4 Paper 2: Spatio-temporal tracer variability in the glacier melt end-member—How does it affect hydrograph separation results?

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My contribution to this article: study design, field work, run mixing model, producing plots, analysing results, and writing article.

Abstract

Geochemical and isotopic tracers were often used in mixing models to estimate glacier melt contributions to streamflow, whereas the spatio-temporal variability in the glacier melt tracer signature and its influence on tracer-based hydrograph separation results received less attention. We present novel tracer data from a high-elevation catchment (17 km², glacierized area: 34 %) in the Oetztal Alps (Austria) and investigated the spatial, as well as the sub-daily to monthly tracer variability of supraglacial meltwater and the temporal tracer variability of winter baseflow to infer groundwater dynamics. The streamflow tracer variability during winter baseflow conditions was small and the glacier melt tracer variation was relatively higher, especially at the end of the ablation period. We applied a three-component mixing model with electrical conductivity (EC) and oxygen-18. Hydrograph separation (groundwater, glacier melt, and rain) was performed for six single glacier melt-induced days (i.e. 6 events) during the ablation period 2016 (July to September). Median fractions (± uncertainty) of groundwater, glacier melt, and rain for the events were estimated at 49±2, 35±11, and 16±11 %, respectively. Minimum and maximum glacier melt fractions at the sub-daily scale ranged between 2±5 and 76±11 %, respectively. A sensitivity analysis showed that the intra-seasonal glacier melt tracer variability had a marked effect on the estimated glacier melt contribution during events with large glacier melt fractions of streamflow. Intra-daily and spatial variation of the glacier melt tracer signature played a negligible role in applying the mixing model. The results of the present study (i) show the necessity to apply a multiple sampling approach in order to characterize the glacier melt end-member and (ii) reveal the importance of groundwater and rainfall-runoff dynamics in catchments with a glacial flow regime.
4.1 Introduction

Large parts of the world are highly dependent on glacial meltwater contribution (originating from ice, snow, firn, and temporally stored rain) to streamflow (Barnett et al., 2005; Kaser et al., 2010; Lemke et al., 2007), especially during dry periods (Frenière and Mark, 2014). Glaciers are important water reservoirs, which have a compensation effect (Lang, 1986). A consistent reduction of global ice mass (IPCC, 2013) may threaten future water usage in a variety of regions and climates. Meltwater originating from glaciers can be seen as a non-renewable water resource under the scope of negative glacier mass balances (Immerzeel and Bierkens, 2012) and accurate assessment of its contribution to basin wide runoff is mandatory for climate change related sustainable water resources management in glacierized watersheds (Miller et al., 2012; Schaner et al., 2012; Viviroli et al., 2011). In the European Alps stream water is often used for irrigation and hydro power generation (Beniston, 2012; Schaefl et al., 2007), as well as for snow making (Rixen et al., 2011). Since mountain streams are composed of water originating from glaciers, snow, rain, and subsurface storages (Cable et al., 2011; Moser and Stichler, 1980; Yde et al., 2016), it is crucial to assess the quantification of streamflow components, to investigate the origin of water, and to improve the understanding of streamflow generation in glacierized catchments under the scope of a changing climate.

Among different and often used methods to quantify the contribution of glacial meltwater to streamflow (i.e. hydrological modelling, direct discharge measurements, hydrological balance equations and glaciological approaches), the tracer-based approach requires the smallest amount of data (Frenière and Mark, 2014) and has relative rarely been used in glacierized environments. By simple mass balances of tracer concentrations in the stream and in the end-members that are forming discharge, the fraction can be determined. The assumption that end-member tracer signatures need to be unique is fundamental for applying this approach, but is often given due to different water origins as a result of hydrological processes in a catchment (Drever, 1997). Tracers applied within this method should be conservative, i.e. no change in signature due to isotopic fractionation or chemical reaction of solutes with geology except due to mixing of different waters (Baraer et al., 2009; Mark et al., 2005). Environmental tracers like electrical conductivity (EC) and stable isotopes of water, such as oxygen-18 ($\delta^{18}O$), have been used in tracer-based hydrologic studies of glacierized catchments (e.g. Engel et al., 2016; Rodriguez et al., 2016; Williams et al., 2016). The spatio-temporal variability in end-members violates the assumption of uniqueness and can be a limiting factor in applying mixing models. The end-member tracer signature variability is crucial for applying mixing models and therefore should be addressed in future studies as Penna et al. (2017) and Frenière and Mark (2014) pointed out. As an example, Penna et al. (2017) advise to define end-member tracer signature dynamically and call for temporal sampling at high frequencies, which was rarely done for the glacier melt or groundwater end-member. Klaus and McDonnell (2013) highlighted the importance of spatial variability in end-member tracer signatures in their review on isotopic hydrograph separation, which should be investigated in future studies. This was also rarely done for glacier melt and the groundwater end-member in high-elevation catchments. The spatio-temporal variation in end-member tracer signatures is
difficult to characterize at the catchment scale (Hoeg et al., 2000), in particular for glacierized catchments (Jeelani et al., 2017), and is affecting mixing model results and uncertainty estimates (Penna et al., 2017). In some studies a limited number of samples (up to 3) was used to characterize the glacier melt end-member (e.g. Kong & Pang, 2012; Liu et al., 2008; Nolin et al., 2010), whereas Maurya et al. (2011) used the average value of 20 samples. Using either a few temporally distributed samples or one average value per melt season value cannot capture the natural spatio-temporal variability and hence potentially leads to an under- or overestimation of the glacier melt fraction and high uncertainties. Recent studies have used a time-variant definition of end-members at the monthly scale (Penna et al., 2017; Wu et al., 2016), whereas others used seasonal average tracer signatures (Liu et al., 2016; Maurya et al., 2011). Penna et al. (2017) pointed out the need for investigating the intra- and inter-annual tracer signature variability of glacier melt.

Meltwater can frequently represent a high proportion (>50 %) of bankfull discharge (Penna et al., 2017). Recent studies estimated glacier melt contributions with tracer-based mixing models in different mountainous regions worldwide up to 70-80 % (e.g. Cable et al., 2011; Kong & Pang, 2012; Penna et al., 2017; Williams et al., 2016). Rainfall contributions to streamflow have often been investigated in temperate humid catchments (Klaus & McDonnell, 2013), but research on rainfall-runoff dynamics in glacierized catchments are rare. Despite melt dominance in those catchments (snow and ice), episodic rainfall events can contribute to streamflow notably (Dahlke et al., 2014). Dahlke et al. (2014) estimated rainfall contributions to streamflow in a 30 % glacierized catchment (21.7 km$^2$) in Sweden at the event scale by up to 58 % during the ablation period in 2011. There exists scarce information on the role of groundwater in glacierized high-elevation catchments and Frenierre and Mark (2014) emphasize to investigate the nexus between dynamics of groundwater and glacier melt contribution to streamflow. Recent studies estimated groundwater fractions at up to 80 % in different mountainous regions with contrasting climates at the event scale (e.g. Baraer et al., 2009; Engel et al., 2016; Wilson et al., 2016).

The variability in the tracer signature of glacier melt is a large source of uncertainty in estimating glacier melt fractions of streamflow (Cable et al., 2011), but important for applying tracer-based hydrograph separation. Here, we quantify its impact on three-component hydrograph separation results and draw implications for further research. The overall scientific objective is to evaluate dynamics of rain, groundwater, and glacier melt contribution to streamflow during melt-induced events in a high-elevation catchment. This study specifically aims 1) to quantify the tracer variability ($\delta^{18}$O, EC) of the end-members groundwater (i.e. winter baseflow) and glacier melt at the sub-daily to monthly scale, as well as at the local scale (only for glacier melt; spatial extent <1400 m), 2) to estimate streamflow fractions and associated uncertainties by tracer-based hydrograph separation and 3) to identify the sensitivity of the hydrograph separation results to the natural spatio-temporal variability of the glacier melt end-member.
4.2 Study area

The study was conducted in the Hochjochbach catchment, a sub-basin of the Rofenache catchment which is a long-term Alpine research site with a comprehensive data set of meteorological, hydrological, and glaciological observations (Strasser et al., 2018). The 17.1 km² high-elevation catchment (Fig. 4-1) is located in the Austrian Alps (N46°46’–N46°49’ / E10°47’–E10°51’), is drained by the Hochjochbach stream, that is trending from southwest to northeast (gauging station at 2450 m a.s.l.), and ranges up to 3520 m a.s.l. (mean altitude: 2950 m a.s.l.). The mean slope is 21°. Two glaciers (Hochjochferner, Kreuzferner) cover an area of 34 %. Mean length change recorded for Hochjochferner is -27 m per year for the period 2007 to 2016 (WGMS, 2017). Mass balance for the Hochjochferner was estimated (glaciological method) at -244 kgm⁻² for the year of 2013/2014 with an Equilibrium-Line Altitude of 3055 m a.s.l. (Prantl et al., 2017). Two tongues of the Hochjochferner are connected with a debris-covered part and their glacier outlet flow directly enters the Hochjochbach stream (cf. Fig. 4-1). The remaining area of the catchment is covered by bedrock outcrops and unconsolidated bare rocks (61 %), as well as by sparsely vegetated area (5 %, alpine meadows) (CLC, 2012). The unconsolidated bare rock area is characterized by glacial deposit (moraine, till), alluvium, alluvial fans, and talus material. The geology consists of paragneiss and mica schist and is overlain by a mantle of glacial deposits and soils (<1 m depth). Mean annual temperature and precipitation at the automatic weather station ‘Latschbloder’ (2920 m a.s.l.) during the water year 2016 (October to September) was -1.66 °C and 1125 mm (54 % as snow, when air temperature <0 °C), respectively. Runoff at the gauging station ‘Bridge’ during the water year 2016 was 1619 mm and is seasonally influenced by snow and glacier melt, clearly indicating a glacial flow regime. Approximately 65 % of annual runoff concentrated between July and September.
4.3 Methods

4.3.1 Event characterization

Six events (#1 to #6) were defined as single glacier melt-induced days during the ablation period (July to September) when most of the snow has disappeared in the catchment (in mid-July there was a patchy snow cover above 3000 m a.s.l. at north-facing slopes which ceased towards early August). The events were characterized by mean daily temperatures >1°C at 2920 m a.s.l., distinct diurnal variation in streamflow (CV > 0.3, except for event #6), low precipitation amounts (<4 mm; rainfall only observed for event #2 and #4), clear sky (during most of the day), and less or equal than 2 mm rain observed 24 h prior to the event (cf. Fig. 4.2b-g). The winter baseflow period (December to March) was characterized by low air temperatures and low variability in discharge, when snowmelt, glacier melt and rain contribution to streamflow is negligible and streamflow is assumed to be supplied by groundwater only.
4.3.2 Hydro-climatologic measurements, sampling design, and tracer analyses

Discharge (hourly values) was measured at the gauging station ‘Bridge’ (at 2450 m a.s.l., cf. Fig. 4-1). The air temperature and precipitation (hourly values) was measured at an automatic weather station (Marke and Strasser, 2017), namely ‘Latschbloder’ (at 2920 m a.s.l., cf. Fig. 4-1). We calculated the antecedent precipitation index (API) for one to seven-day periods to capture a wide range of moisture conditions and to relate it to the rainfall fraction in streamflow. In the next step we chose API$_2$ and API$_7$ for further analyses (for correlation analyses see Chapter 4.4.3) to capture various wetness conditions for each of the events and to make sure that every event receives a remarkable amount of rainfall (i.e. an arbitrary threshold of 19 mm). Furthermore the selection of API$_2$ and API$_7$ allows for a comparison between conditions which occurred close and not-so-close to an event.

Streamflow was sampled manually (grab samples) at the gauging station ‘Bridge’ (n=19 in total) during the events. 2 to 5 samples between 09:00 and 16:00 (CET) were collected at 1- to 5-hourly intervals per event. Winter baseflow samples (n=14) were collected at the same location on 22 December 2015, 28 January, and 17 March 2016. The samples of 17 March 2016 (9 out of 14) were collected at a 30-minute interval between 11:30 and 15:30 (CET) to identify the potential sub-daily variability in the tracer signature. Supraglacial meltwater (n=51 in total) was sampled approximately every 100 to 200 m along a contour line parallel transect (A1 to A5, see inlay in Fig. 4-1) on the ablation area during four field days (event #1 to #4) at approximately 12:30 (CET) to investigate the spatial and the intra-seasonal variability of glacier
melt. During two events (#5 and #6) supraglacial meltwater was sampled approximately every 50 to 250 m along contour line parallel transects (2 transects per sampling day with 3 samples per transect, A1 to A3, B1 to B3) at 10:00, 13:00 and 15:30 (CET) to include a potential sub-daily variability and a larger spatial range (cf. Fig. 4-1). Rain (n=9 in total) was sampled by collectors at two sites (‘Bridge’ and ‘Glacier’, cf. Fig. 4-1) during the study period when liquid-phase precipitation occurred and represents bulk values. The polyethylene collectors (Ø: 10 cm) were filled with a 0.5 cm mineral oil layer to prevent evaporation and were installed at 1.20 m above the surface. Rain samples were recovered on 23 June 2016 and during each of the events (for dates please see Fig. 4-2).

EC was measured with a portable probe (WTW ProfiLine Cond 3310) with temperature compensation (25°C) in situ. The measurement precision is 0.1 µScm\(^{-1}\). Water samples collected in the field were stored in dark and cold in high-density polyethylene bottles until analyses for δ\(^{18}\)O with cavity ring-down spectroscopy (Picarro L1102-i) in the laboratory. The measurement precision is 0.1 ‰.

4.3.3 Hydrograph separation and uncertainty analyses

Hydrograph partitioning with environmental tracers is based on mass balances of water (Eq. 4-1) and tracers (Pinder and Jones, 1969). A two-tracer, three-component mixing model (Ogunkoya and Jenkins, 1993) was applied to partition the streamflow \(Q_t\) into the groundwater \(Q_g\), rain \(Q_r\), and glacier melt component \(Q_m\). A successful separation of streamflow requires that: 1) tracer signatures of water sources differ significantly; 2) contributing water sources maintain constant tracer signatures, or their variability can be quantified; 3) streamflow is composed solely of those three components; 4) tracers mix conservatively (a comprehensive description of model assumptions can be found in: Buttle, 1994; Hinton et al., 1994; Klaus and McDonnell, 2013; Rodhe, 1987).

\[
Q_t = Q_g + Q_r + Q_m \quad (4-1)
\]
\[
Q_t \delta_t = Q_g \delta_g + Q_r \delta_r + Q_m \delta_m \quad (4-2)
\]
\[
Q_t c_t = Q_g c_g + Q_r c_r + Q_m c_m \quad (4-3)
\]

Eq. 4-2 and Eq. 4-3 show the resulting mass balances of water and tracer fluxes. Input for Eq. 4-2 are EC values of total streamflow \(C_t\) and the conceptual water sources (end-members) groundwater \(C_g\), rain \(C_r\), and glacier melt \(C_m\). \(\delta_t\), \(\delta_g\), \(\delta_r\), and \(\delta_m\) represent the δ\(^{18}\)O composition of total streamflow, groundwater, rain, and melt for Eq. 4-3, respectively.

Winter baseflow was assumed to reflect and integrate the hydrochemistry of (shallow) groundwater, as used in other studies (e.g. Fischer et al., 2016; Klaus and McDonnell, 2013; Penna et al., 2017; Sklash, 1990). Hence the groundwater end-member is characterized by the mean tracer signature of winter baseflow. The rain end-member was characterized by the rain samples. For the days where two bulk samples could be obtained, they were volume-weighted with rain depths to incorporate the spatial variability. To account for the temporal variability and slower flow paths of rain routing through the subsurface, the incremental mean intensity
method after McDonnell et al. (1990) was applied for the mixing model. The glacier melt end-member is characterized by the tracer signature of supraglacial meltwater samples and can constitute of ice melt, firn melt, snowmelt and temporally stored rain. Since glacier melt sampling was conducted mainly during rain-, snowmelt- and firn melt-free periods, we assume ice melt to be the dominant component. In order to reveal the effect of the varying glacier melt tracer signature on the estimated glacier melt fraction we performed a sensitivity analysis and characterised the glacier melt end-member temporally variable at the event scale (approach A), seasonally time-invariant (approach B), temporally variable at the sub-daily scale (approach C, sub-daily data was only for event #5 and #6 available), and also spatially variable in approach D (Tab. 4-1). A time-invariant baseflow tracer signature and a time-variant rain end-member characterization were used for all approaches (as described above). We assumed a negligible snowmelt contribution to streamflow, except that originating from the glacier surface. During field work in July this assumption was visually ensured as the winter snowpack has almost disappeared on bare ground (cf. Chapter 4.3.1). Intermittent snowfall events were assumed to have a small snow water equivalent and negligible influence on the analyses.

For the uncertainty analysis the Gaussian error propagation method (Genereux, 1998) with a confidence level of 95 % was applied. Factors including the spatio-temporal variability of the end-members, as well as the laboratory uncertainty were taken into account. The spatio-temporal variability was accounted for by using the standard deviation of tracer signatures in the samples collected at different locations over time. According to the device manuals (measurement precision), 0.1 µS cm⁻¹ and 0.1 ‰ were used as the laboratory uncertainty in the analyses for EC and δ₁⁸O, respectively.
4.4 Results

4.4.1 Hydro-climatological conditions
The winter baseflow period (December to March, Fig. 4-2a) was characterized by an average discharge of 0.06 m³ s⁻¹ and a small variation in discharge (CV=0.24). The average air temperature was -7.1°C and the observed precipitation sum (approximately 95% as solid phase) was 268 mm during this period (Tab. 4-2). The six investigated events during the ablation period (July to September) were characterized by distinct diurnal cycles in air temperature and discharge (Fig. 4-2b-g). The highest variation in discharge was observed for event #5 (CV=0.66). Mean values for event air temperature ranged between 1.9 °C (for event #6) to 8.9 °C (for event #1). Average event discharge was between 0.40 (event 6#) and 2.79 m³ s⁻¹ (event #4). A significant correlation was observed between discharge and air temperature for the events #1 to #5, with Spearman correlation coefficients ranging between 0.39 (event #3) to 0.59 (event #4) at the 10% significance level (Tab. 4-2). Events #1, #3, #5 and #6 were rain-free and all events were at least dominated by clear sky and high radiative energy input. Rainfall was observed during event #4 (3.9 mm) and event #2 (0.9 mm). API₂ was highest for event #4 (15.3 mm) and smallest for event #1 and #2 (0.2 mm). Maximum API₂ was observed for event #1 (58.9 mm) and a minimum value was observed for event #6 (18.9 mm, Tab. 4-2).
4.4.2 Tracer variability in water sources and streamflow

All analysed water samples are split into water sources (glacier melt, groundwater, rain) and streamflow in Fig. 4-3. Rain δ¹⁸O values are relatively higher compared to glacier melt, groundwater and streamflow δ¹⁸O values (Fig. 4-3a). Rain isotopic values are significantly different from glacier melt (Kruskal-Wallis test: p<0.001) and groundwater (Kruskal-Wallis test: p=0.002). Fig. 4-3b displays low EC values for rain and glacier melt, high ones for groundwater and intermediate ones for streamflow. There are significant differences in EC between each of the three water sources observed (pairwise Wilcoxon test with post-hoc Bonferroni correction: p<0.001). The groundwater (winter baseflow) tracer signatures (n=14) were spread between -14.7 and -14.5‰ (median=-14.6‰) for δ¹⁸O and between 175.2 and 186.0 µS cm⁻¹ (median=184.1 µS cm⁻¹) for EC. The variation throughout the December to March period, as well as for an intense sampling day on 17 March (n=9, 30-min interval) was small for both analysed tracers (Fig. 4-3, Tab. 4-3). Values for EC range from 4.7 to 14.5 µS cm⁻¹ (median=7.4 µS cm⁻¹). δ¹⁸O data ranges between -17.7 to -5.3‰ (median= -8.8‰). Streamflow samples (n=19) collected during the events were varying between -14.1 and -13.4‰ (median= -13.8‰) for δ¹⁸O and between 45.8 and 158.3 µS cm⁻¹ (median= 89.4 µS cm⁻¹) for EC. Discharge reveals a strong relationship to tracer signatures of streamflow (Fig. 4-4a and b). The discharge is positively correlated with δ¹⁸O (Kendall’s Tau: τ=0.69, p<0.001) and negatively with EC (Kendall’s Tau: τ=-0.58, p<0.001). Data for event #6 (green circles) stand out for both relationships and is characterized by relatively low discharge and relatively high EC and low δ¹⁸O values. This data therefore form a distinct cluster.
Glacier melt samples (n=51, Tab. 4-3, Fig. 4-5) ranged from -17.0 to -12.2 ‰ in δ¹⁸O (median= -14.7 ‰) and from 1.3 to 10.1 µScm⁻¹ in EC (median= 2.1 µScm⁻¹). The inter-event variability was marked for both EC and δ¹⁸O, and medians of event #6 values were statistically different to most of the remaining event values at the 10 % significance level (pairwise Wilcoxon test with post-hoc Bonferroni correction). The temporal intra-event variability (data from event #5 and #6) was significantly different for EC on 13 September (10:00 and 13:00 values differed with p=0.003), but not for δ¹⁸O. Kruskal-Wallis tests on medians of different sampling sites for event #1 to #4 (sampling sites A1 to A5) and for events #5 and #6 (sampling sites A1 to B3) revealed no statistical significant difference for EC and δ¹⁸O. Tests in tracer signature differences for both investigated glacier tongues (A, B, cf. Fig. 4-1) revealed no statistical significant differences (Kruskal-Wallis for EC and δ¹⁸O). The temporal variation and the spatial variation between the sampling locations in tracer signatures of glacier melt are displayed in Fig. 4-6. There is no clear spatial pattern observable and the color variation along the x-axis (i.e. temporal variability) seems to be larger compared the one along the y-axis (i.e. spatial variability). EC values (Fig. 4-6b and d) display at the lower
end of the color range (more blueish pixels) while $\delta^{18}O$ values seem to cover the color range (from blue to red) more evenly distributed over the whole observation period (Fig. 4-6a and c). The glacier melt $\delta^{18}O$ values at A1 on 13 September (reddish pixels in Fig. 4-6c), as well as the higher varying EC values on 22 September (blue to red pixels in Fig. 4-6d) compared to the remaining EC values stand out.

Fig. 4-5: $\delta^{18}O$ (a) and EC (b) signatures of glacier melt during the investigated events.

Fig. 4-6: Spatio-temporal pattern of glacier melt sampled on event #1 to #4 for $\delta^{18}O$ (a) and EC (b), and $\delta^{18}O$ (c) and EC (d) glacier melt signatures for event #5 and #6. Grey pixels indicate missing data.
4.4.3 Hydrograph separation results and their uncertainties

The end-members glacier melt, groundwater and rain span a triangle around the stream samples in the EC-$\delta^{18}$O mixing space and allow for applying a three-component mixing model (Fig. 4-7; end-member values for the different events are shown in Tab. 4-6 in the supplement). The event #6 streamflow samples (green circles) group apart from the main cluster (event #1 to #5) and are located closer to the groundwater end-member in the mixing space. Fig. 4-8 displays the average streamflow component fractions and associated uncertainties per event, estimated with the mixing model and approach A (mean glacier melt end-member tracer signature per event). It becomes obvious that streamflow is composed differently in each event and this reflects the variability throughout the ablation period. The lowest mean glacier melt fraction was observed for event #6 (5±5 %) and was accompanied by the lowest air temperatures (mean daily air temperature: 1.9 °C). The highest mean glacier melt fraction was observed for event #2 (69±10 %), concomitant with the highest runoff (14 mm). The median glacier melt fraction of all 6 events was 35±11 %. The average rain fraction of streamflow per event ranged between 0±10 % (event #2) and 23±6 % (event #4) with a median of 16±11 % for all events. The mixing model applied for event #2 revealed no rain contribution to streamflow. Hence we conducted a two-component hydrograph separation with EC (Pinder & Jones, 1969) for event #2 which revealed a mean glacier melt fraction of 69±2 %. The maximum rain contribution (24±6 %) was observed during event #4 (12:00 CET). The median groundwater contribution to streamflow for all events was 49±2 %. Mean fractions per event ranged between 31±2 (event #2) to 81±3 % (event #6). A maximum fraction (86±4 %) was estimated for event #6 (11:00 CET) and a minimum fraction (24±1 %) for event #2 (14:00 CET). The glacier melt fraction was also varying at the sub-daily scale (Fig. 4-9). The glacier melt fraction shows a similar pattern for each event, i.e. an increase over the course of the day with a maximum range observed for event #5 (increase from 24±11 to 48±20 %). Sub-daily glacier melt fractions ranged between 2±5 % (22 September 11:00 CET) and 76±11 % (30 July 14:00 CET) and the highest uncertainty was estimated for event #5 (up to ±20 %).
Fig. 4-7: EC-$\delta^{18}$O mixing plot. The end-members (rain, glacier melt, groundwater) are represented by mean values (error bars indicate the standard deviation) and span a triangle around the streamflow samples.

Fig. 4-8: Average streamflow component fraction and uncertainty (error bars) per event (estimated with approach A).
Fig. 4-9: Glacier melt fraction and uncertainty (error bars) estimated with approach A. Please note that x-axis scale is not continuous.

Fig. 4-10 shows the sensitivity of the estimated glacier melt fractions to the sampling time of glacier melt (approach C). The variations are not marked and the values are close to the approach A values (represented by crosses in Fig. 4-10), but event #5 (13 September) reveals a slightly higher spread compared to event #6 (22 September). During event #5 the glacier melt sampling time before noon (10:00 CET) led to slightly higher glacier melt contributions compared to the average value (approach A; for the exact values see Tab. 4-4 in the supplement). Fig. 4-11 highlights the sensitivity of the estimated glacier melt fractions to the sampling location of glacier melt (approach D). Overall, the scatter around the average value (results from approach A) is limited (<7 % absolute difference), except for event #1 (sampling location A5) and event #5 (sampling location A1) an outlier appears. A maximum absolute difference of +15 and +24 % for both events was calculated, respectively (exact values are shown in Tab. 4-5 in the supplement). Fig. 4-12 shows the glacier melt contribution to streamflow and associated uncertainties estimated with approach B (mean seasonal glacier melt end-member tracer signature) against those estimated with approach A (mean event glacier melt end-member tracer signature). Glacier melt fractions estimated with approach B revealed on average 5 % lower glacier melt fractions compared to those of approach A. Glacier melt fractions estimated with approach B revealed similar estimates (close to the 1:1 line in Fig. 4-12) for event #1, #4, #5, and #6. Maximum deviations were observed for event #2 and #3 (-17 % of approach A value).
Fig. 4-10: Sensitivity of estimated glacier melt contribution to sub-daily glacier melt end-member characterization (approach C) for event #5 and #6. Crosses represent glacier melt fractions estimated with approach A. Please note that x-axis scale is not continuous.

Fig. 4-11: Sensitivity of estimated glacier melt contribution to the glacier melt sampling location (approach D). Red stars represent glacier melt fractions of approach A. Please note that x-axis scale is not continuous.
The mean rain fraction of streamflow during the events is positively correlated with API$_2$ (Kendall’s Tau: $\tau=0.73$, $p=0.06$), but not with API$_1$. The rain fraction of streamflow has a positive relationship with $\delta^{18}$O (Kendall’s Tau: $\tau=0.54$, $p<0.001$), but none with EC. The groundwater fraction of streamflow is correlated with EC (Kendall’s Tau: $\tau=0.99$, $p<0.001$) and $\delta^{18}$O (Kendall’s Tau: $\tau=-0.52$, $p<0.001$). The mean fraction of glacier melt during the event is positively correlated with mean event air temperature (Kendall’s Tau: $\tau=0.73$, $p=0.06$). The relationship between glacier melt fraction (approach A) and streamflow tracer signatures is displayed in Fig. 4-13a and b. The glacier melt fraction is positively correlated with streamflow $\delta^{18}$O (Kendall’s Tau: $\tau=0.32$, $p=0.06$) and negatively correlated with EC (Kendall’s Tau: $\tau=-0.81$, $p<0.001$). The data in the scatterplot show the event-wise grouping for both tracers (see color-coding of the events).
4.5 Discussion

4.5.1 Tracer variability in water sources and streamflow

The spatio-temporal variability in tracer signatures of water sources represents a large source of uncertainty in applying mixing models (Pu et al., 2013; Uhlenbrook and Hoeg, 2003). Therefore adequate sampling strategies (e.g. not sampling peak flow or sampling during wet antecedent days potentially leads to underestimated glacier melt fractions) are necessary for the planning of field campaigns, as already noted by Penna et al. (2017). Sampled water sources (glacier melt, rain, and winter baseflow as a proxy for shallow groundwater) revealed significant differences in EC and marked differences in \( \delta^{18}O \) (Fig. 4-3). EC is a proxy for total dissolved solids and was relatively high in shallow groundwater. This suggests that the catchment hydrology is dominated by slower, subsurface flow paths of water during the December to March period. Little variation in \( \delta^{18}O \) values of stream discharge (-14.7 to -14.5 ‰) during this period also supports the evidence of a well-mixed groundwater reservoir which supplies winter baseflow similar to Ambach et al. (1976), Penna et al. (2017) and Rodriguez et al. (2016). Lower EC values were observed in the Hochjochbach stream during the summer ablation period (July to September) compared to the EC values during the winter baseflow period (Fig. 4-3b). Higher EC values during winter and lower values in summer are typical for glacierized catchments (e.g. Penna et al., 2017). This indicates marked contributions of glacial meltwater, which is typically diluted in solutes (Fig. 4-3b). During the events (July to September) streamflow \( \delta^{18}O \) varies between -14.1 and -13.4 ‰, and indicates changing contributions of water sources with different signatures. Analogously the varying EC content of streamflow (range: 45.8-158.3 µS cm\(^{-1}\)) indicates the contribution of high EC groundwater or the low EC rain/glacier melt component, under the assumption of homogenous geology and flow paths. The negative relation between discharge and streamflow EC (dilution effect) in melt-dominated catchments was already intensively studied (Collins and Young, 1981; Dzikowski and Jobard, 2012; Engel et al., 2016) and was also significant within this study (Fig. 4-4b). A significant positive relationship of discharge and streamflow \( \delta^{18}O \) was found (Fig. 4-4a). Spatio-temporal variation in rain isotope signatures (Fig. 4-3a) is observed (range between -17.7 and -5.3 ‰), but is not of the main interest in this study. EC of rain varies between 4.7 and 14.5 µS cm\(^{-1}\), most likely varying due to air masses originating from Mediterranean (favours more salty rain and higher EC values) or Atlantic (favour less salty rain and lower EC values) moisture sources. Variations in EC of rain may also occur due to atmospheric deposition (e.g. dust). Penna et al. (2014) also observed a similar range in EC of rain in a catchment close to our study area.

The sample size (n=51 in total) of this study to characterize the glacier melt tracer signature is one order of magnitude greater compared to most other studies, and therefore allows to draw a solid conclusion on the temporal and spatial variability (at the local scale). The temporal variability in glacier melt tracer signature was higher compared to the spatial variability. The intra-seasonal variation was larger compared to the within-day variation for \( \delta^{18}O \). A decreasing tendency in the isotopic composition of glacier melt from event #2 to #6 is visible, which is contrary to the findings of Penna et al. (2017) and Yde et al. (2016), who observed an increase
in glacier melt isotopic signatures during the ablation period. Other authors found no intra-seasonal variability in glacier melt tracer signatures (Cable et al., 2011; Maurya et al., 2011; Ohlanders et al., 2013; Racoviteanu et al., 2013). The within-day variability in EC and δ¹⁸O was marked for event #6, however this variability was not observable during the other events (Fig. 4-5). The high variation is likely related to an intermittent snowfall event, where a thin layer (<2 cm) of new snow covered the Hochjochferner (all snow was melted in the afternoon). Typically, snow is characterized by lower δ¹⁸O values due to the temperature effect (Dansgaard, 1964). The intra-daily variation in EC of glacier melt on 22 September was likely caused by the dilution effect. Due to the low radiative energy input, the resulting melt rate was low in magnitude which was visually ensured. At 10:00 (CET) when melt was minimal, meltwater draining from the abovementioned new snow on the glacier surface, which is typically higher in EC compared to glacier meltwater (Fountain, 1996), led to relatively high EC values (yellow to reddish pixels in Fig. 4-6d). These became progressively lower with a minimum at 15:30 (CET) in the afternoon when the melt rate was highest. Jeelani et al. (2017) found higher EC values in meltwater originating from a debris-covered glacier compared to a clean glacier. Since glacier melt tracer signatures depend on the water origin (e.g. supraglacial meltwater vs. glacier outflow), the origin of the air masses that form precipitation, and the post-depositional processes, a direct comparison is solely valuable for catchments with similar climate conditions and physical characteristics. As an example Penna et al. (2014) sampled rivulets on the glacier surface in a catchment close to the Hochjochbach catchment and revealed medians of approximately -14 ‰ and 5 µS cm⁻¹ for δ¹⁸O and EC (extracted from figure), respectively, which are close to our values. A small spatial variation, but a marked intra-seasonal pattern in the tracer signature of glacier melt was observed by Penna et al. (2017). A clear intra-seasonal enrichment of glacier melt isotope values could not be identified within the present study, but a variation that should be accounted for in mixing models was observed (Fig. 4-5). The spatial variation was negligible (Fig. 4-6), but should be investigated at a larger spatial scale, although assumptions exist on missing isotope variability of different glaciers within a catchment (Cable et al., 2011). Zhou et al. (2014) found no clear altitude gradient in the isotopic signal of glacier melt, whereas Wu et al. (2016) found an altitude effect (-0.34 ‰/100 m for δ¹⁸O). For the Hochjochferner this would result in a total change of -2.38 ‰/700 m. This effect, if observed, would play a minor role since the value lies within the observed range of the Hochjochferner glacier melt values and most of the glacier melt originates from the ablation area (glacier tongue), where the sampling was conducted. Despite our efforts to capture the variability in the glacier melt tracer signature, identification of it at a larger spatial scale (sampling various glaciers in a catchment >20 km²) remains an open issue. Future work is also required in estimating the interannual variability of the glacier melt tracer signature.

4.5.2 Hydrograph separation results and their uncertainties

In a variety of mountain catchments worldwide and different mixing model settings, subsurface water, rain and melt contributions to streamflow at the seasonal scale were quantified by 2-76, 20-22, and 13-53 ‰, respectively (e.g. Cable et al., 2011; Zhou et al., 2015). Nevertheless, those studies are often hard to compare due to (i) different glacier melt
definitions (Frenierre & Mark, 2014), (ii) differences in glacierized area, (iii) climate variability, (iv) spatio-temporal scale issues (Penna et al., 2017), (v) varying characterization of end-members (e.g. predetermined or determined by geochemical streamflow data), and (vi) sampling of different components (e.g. sampling glacial outflow vs. supraglacial meltwater to characterize the glacier melt end-member or sampling winter baseflow vs. spring water to characterize the groundwater end-member).

Glacier melt fraction in streamflow and its sensitivity to the glacier melt end-member characterization

The median glacier melt contribution to streamflow for six events during July to September was 35±11 %, and is in the range of seasonal glacier melt contributions (28-59 %) estimated in other studies for similar catchments (Cable et al., 2011; Engel et al., 2016; Penna et al., 2017). If one assumes that annual glacier melt contribution occurs solely within the July to September period and runoff constitutes of 35 % glacier melt (367 mm) during that period, glacier melt contributes approximately 23 % to annual runoff (1619 mm) in the Hochjochbach catchment (October 2015 to September 2016). Maximum event contribution was 69±10 % (event #2) and compares well with maximum estimates from Penna et al. (2017) and Engel et al. (2016) at the event scale (71 and 65 %, respectively). This represents the importance and dominance of the glacier melt streamflow fraction in headwater catchments during summer in the Alps and future changes in glacial meltwater contribution in that region are likely (Hanzer et al., 2018). A dominant role of glacier melt in summer and late summer streamflow was also observed in the Rocky Mountains (Cable et al., 2011), Andes (Ohlanders et al., 2013), and the Arctic (Blaen et al., 2014). In this study a decreasing pattern in glacier melt fraction was observed from 30 July (69±10 %, event #2) to 22 September (5±5 %, event #6). This dynamic behaviour was contrary to the findings of Williams et al. (2016) and Racoviteanu et al. (2013) who revealed an increase in glacier melt contribution for the July to September period in the Himalaya. Our observed pattern could be related to the observation period, starting when snow cover was almost depleted and annual peak glacier melt likely occurred close to the beginning of the summer sampling work (end of July) and was followed by a subsequent recession of the glacier melt contribution. Penna et al. (2017) also observed most of the glacier mass loss between end of July and mid-August. Further estimates on the interannual glacier melt contribution variability are required. The relatively high uncertainty during event #5 (up to ±20 %; see Fig. 4-9) is likely caused due to a combination of the highly varying glacier melt $\delta^{18}$O signature and a high glacier melt fraction (up to 48 %), both affecting the uncertainty estimation (cf. Genereux, 1998). The mixing model results were partly sensitive to the characterization of the glacier melt end-member. Using the seasonal average of the glacier melt tracer signature for applying the mixing model (approach B) led to underestimated glacier melt fractions (average: -5 %) compared to the use of the event mean glacier melt tracer signature (approach A), especially when glacier melt was the dominant contributor. Hence, the highest deviation was observed for event #2 and #3 (-17 %). We infer that it is necessary to use a time-varying glacier melt end-member at least at the sub-seasonal scale as already done recently by Penna et al. (2017) and Wu et al. (2016) at the monthly scale. Furthermore our data show that it is important to incorporate the temporal variability of glacier melt tracer signature
below a monthly resolution, because the δ¹⁸O values to describe the glacier melt end-member (Fig. 4-5) varied from event to event. However, the sensitivity of the glacier melt contribution to the sub-daily characterization of the glacier melt end-member (approach C) is not marked. There is a small deviation observable if one samples glacier melt in the morning (10:00 CET) (event #5 in Fig. 4-10). This effect is caused by the higher δ¹⁸O values (yellow pixels in Fig. 4-6c) compared to those at 13:00/15:30 (CET). This was not the case for event #6 and we want to point out that those two events are likely not sufficient to draw a general conclusion of such an emergence as observed for event #5. Hence we hypothesize that the sub-daily variation of the glacier melt end-member tracer signature may not be important, but further data from different catchments is absolutely needed to test it. The sensitivity of the glacier melt estimations to the spatial variability of the glacier melt tracer signature (Fig. 4-11) is also not marked, but two outliers (sampling locations A1 and A5) become obvious. Both, for event #1 the sampling location A5 and for event #5 the sampling location A1, led to markedly higher glacier melt estimates compared to the average value. Both cases were caused by high δ¹⁸O values (cf. Fig. 4-6). We cannot explain the abovementioned outliers, but our data showed that sampling either at different locations on the ablation area, or sampling both tongues of the glacier (cf. Fig. 4-1 and Chapter 4.2) does not seem to be of particular importance. The correlation of the glacier melt fraction of approach A and the streamflow tracer signature was significant for both δ¹⁸O and EC at the 10 % significance level (Fig. 4-13). The observed relationship is stronger for the glacier melt fraction and streamflow EC, similar to the dilution effect described in other studies (e.g. Dzikowski & Jobard, 2012). The less strong relationship between streamflow δ¹⁸O and the glacier melt fraction (Fig. 4-13a) could likely be attributed to the similarity of the glacier melt and the groundwater δ¹⁸O values (cf. Fig. 4-3 and Tab. 4-3). However, data for event #1 to #3 seem to deviate from the relationship for both, EC and δ¹⁸O.

**Groundwater fraction in streamflow and its end-member characterization**

Groundwater, characterized by the winter baseflow tracer signature was the dominant contributor to streamflow (49±2 %) for the studied six melt events during the period July to September 2016. At the event scale we observed an increase in groundwater contribution to streamflow from event #2 (31±2 %) to event #6 (81±3 %) that is inversely related to the glacier melt contribution. Engel et al. (2016) determined groundwater contribution up to 62 % for melt events analysed in a small headwater catchment (12 % glacierized area) in the Alps and found that groundwater was the major streamflow component for 7 observed melt events (38 to 62 %). Penna et al. (2017) investigated a tendency of increasing groundwater contribution between July and September in the same catchment, with a maximum contribution >80 % (approximate value extracted from figure). Large groundwater contributions and its storage in soils and unconsolidated sediment (such as talus, moraines, alluvium, alluvial fans, and rockslides) are frequently observed in high-elevation catchments and likely play a major role for future water supply, especially under changing climatic conditions and system states of those catchments (Jasechko et al., 2016; Staudinger et al., 2017). Baseflow is a combination of shallow and deep groundwater (Ward and Robinson, 2000), can have long residence times (Ambach et al., 1976; Stewart & McDonnell, 1991), and
is a mixture of snowmelt, rain, and glacier melt, as quantified by Cable et al. (2011). There was an intense discussion on the characterization of the subsurface end-member as condensed by Buttle (2006). Characterizing the groundwater end-member by the tracer signature of (winter) baseflow can be more reliable than using averaged spring water, because the isotopic and geochemical signature of streamflow during baseflow conditions is known to integrate and represent the hydrochemistry of (shallow) groundwater at the catchment scale (Fischer et al., 2015; Kendall and Doctor, 2003; Klaus and McDonnell, 2013; Sklash, 1990). Nevertheless using winter baseflow instead of average spring water tracer signatures could lead to underestimated glacier melt fractions, as shown by Penna et al. (2017). We considered winter baseflow tracer signature to characterize the groundwater end-member, as used elsewhere (e.g. Miller et al., 2016). Since small mountainous headwater catchments typically tend to favour shallow subsurface flow paths (Frisbee et al., 2011), while deeper longer flow path bypass first-order (headwater) streams through fractured bedrock and supply stream water at a larger scale downstream (Gleeson and Manning, 2008), the groundwater end-member is considered to represent shallow subsurface flow in this study. Unconsolidated material such as glacial deposit, moraine, till, and loose rock of talus slopes likely functions as storage of this water source, that is not negligible in high-elevation catchments as the Hochjochbach basin. Accounting for the temporal variation of the groundwater tracer signature is difficult, but a distinct variation could not be shown within this study. Therefore the use of the (time-invariant) average tracer signature of winter baseflow during the December to March period seemed reliable to characterize the groundwater end-member.

Rain fraction in streamflow and inferred runoff mechanisms

The median rain fraction in streamflow during the six investigated events was estimated at 16±11 %. Minimum and maximum event contribution was 0±10 % (event #2) and 23±6 % (event #4). Dahlke et al. (2014) investigated rainfall-runoff events in a 30 % glacierized catchment (21.7 km²) in Northern Sweden with very similar characteristics and climate as the Hochjochbach catchment using a two-component hydrograph separation with δ¹⁸O. The event water end-member was characterized by rain samples and was on average 11 and 22 % for two non-consecutive ablation periods, depending on interplay between the rainfall event timing, snow cover and soil moisture conditions. Related rain contributions during melt-induced events are very rare hence a comparison is hampered. As an example Engel et al. (2016) estimated a marked rain contribution of 11 % for a rainfall-runoff event (<10 mm d⁻¹ precipitation) by a two-tracer (EC and δ¹⁸O) three-component mixing model (rain, glacier melt, groundwater), well comparable to our results and highlighting the importance of rain contribution in glacierized catchments. It should be mentioned that our results were related to antecedent rainfall. Since rainfall-runoff dynamic was not the major part of interest in this study and sampling was conducted on almost rain-free events (except on event #2 and #4 rainfall occurred, but sampling on those days was finished before) our estimated rain fractions in the streamflow are not negligible. The correlation analysis of the 2-day antecedent rainfall sum and the rain fraction of streamflow were significant and support the assumption of longer transit times (longer than one day as assumed for the glacier melt end-member). 2-day residence time is short, but seems reasonable due to thin soils and unconsolidated material.
(deposit, moraine) which likely favours a higher hydraulic conductivity (Weiler et al., 2005). Baraer et al. (2015) underscored in their Andean catchment the importance of groundwater contribution in proglacial regions and suggested talus deposits as controlling landscape features which regulate shallow groundwater movement and routing of rain water through the subsurface. This is also typical for the Hochjochbach catchment. Therefore including the rain component is crucial in glacierized catchments. Furthermore the EC-$\delta^{18}$O mixing diagram (Fig. 4-7) indicates that streamflow tracer signature cannot be explained by using one tracer only (streamflow samples display not on a line between two water sources). Glaciers are known to have a low retention capacity for rain water (especially if the snow cover is depleted) and provide a fast routing of rainwater to the stream (Dahlke et al., 2014). Due to this fact and the investigation of antecedent (not event) rainfall-runoff dynamics, we must conclude that catchment storage (not glacier storage) is the key to better understand rainfall-runoff dynamics in glacierized catchments at the larger than 1-day scale. Future work on the relation between rainfall and runoff should be conducted in those environments.

4.6 Conclusion

In this study we presented novel research including 1) winter baseflow tracer variation in a glacierized catchment, 2) high temporal and spatial resolution of the glacier melt tracer signature (large dataset), and 3) tracer-based streamflow partitioning (glacier melt, rain, groundwater) and its sensitivity to the glacier melt tracer variability. Our work is representative for headwater catchments (30-40 % glacier coverage) with a glacial flow regime. We investigated six melt-induced events during the ablation period from July to September 2016 in a 17.1 km$^2$ catchment (34 % glacierized area) in the European Alps and assessed the spatio-temporal variability of end-member tracer signatures ($\delta^{18}$O, EC). The winter baseflow tracer signatures served as a proxy for shallow groundwater and revealed a very small variation, supporting the evidence of a well-mixed reservoir. The temporal tracer variation of glacier melt (EC and $\delta^{18}$O) is marked at the sub-seasonal scale (July to September) and is more pronounced for $\delta^{18}$O. Sub-daily and spatial variation plays a minor role, but also variations in $\delta^{18}$O are more pronounced. The glacier melt fraction at the daily (event) scale ranged between 5±5 and 69±10 % (median: 35±11 %), with an annual contribution of 23 %, that likely represents the lower threshold. Groundwater (median: 49±2 %) was the dominant contributor during the investigated events, likely becoming more important due to further retreat of the glacier and expected future decrease in the glacier melt contribution. Antecedent rain played a minor, but not negligible role (median: 16±11 %). We have shown, that including a time-variant glacier melt end-member characterization (if possible at the sub-monthly scale) in mixing models is important, since using a time-invariant glacier melt tracer signature led to 5 % lower glacier melt fractions on average and up to 17 % underestimation per event. Spatial (at the scale of 100 of meters) and sub-daily variation in the glacier melt end-member tracer signature revealed no distinct effect on the mixing model results.
Acknowledgements

This work is part of the project HydroGeM³ and has been funded by the Austrian Academy of Sciences. We gratefully thank Nora Els, Tobias Horn, Felix Heinz, and the volunteers for their help during the field work. We also acknowledge the Center of Stable Isotope Analysis (CSI) at the Karlsruhe Institute of Technology (Institute of Meteorology and Climate Research - Atmospheric Environmental Research) for the water stable isotope analyses.
Tab. 4-4: Glacier melt fraction and uncertainty (in %) estimated with approach C. Times are in CET.

<table>
<thead>
<tr>
<th>Streamflow sampling time</th>
<th>10:00</th>
<th>13:00</th>
<th>15:30</th>
<th>Daily average (approach A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Event #5 (13 Sep) 09:00</td>
<td>26±15</td>
<td>25±13</td>
<td>25±13</td>
<td>24±11</td>
</tr>
<tr>
<td>10:30</td>
<td>28±16</td>
<td>26±14</td>
<td>26±14</td>
<td>25±12</td>
</tr>
<tr>
<td>12:00</td>
<td>32±19</td>
<td>31±16</td>
<td>30±16</td>
<td>30±13</td>
</tr>
<tr>
<td>15:00</td>
<td>45±26</td>
<td>44±22</td>
<td>43±23</td>
<td>43±18</td>
</tr>
<tr>
<td>16:00</td>
<td>49±29</td>
<td>48±24</td>
<td>47±25</td>
<td>48±20</td>
</tr>
</tbody>
</table>

Tab. 4-5: Glacier melt fraction and uncertainty (in %) estimated with approach D.

<table>
<thead>
<tr>
<th>Glacier melt sampling location as used for mixing model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Streamflow sampling time</td>
</tr>
<tr>
<td>-------------------------</td>
</tr>
<tr>
<td>Event #1 (19 Jul)</td>
</tr>
<tr>
<td>Event #2 (30 Jul)</td>
</tr>
<tr>
<td>Event #3 (08 Aug)</td>
</tr>
<tr>
<td>Event #4 (31 Aug)</td>
</tr>
<tr>
<td>Event #5 (13 Sep)</td>
</tr>
<tr>
<td>Event #6 (22 Sep)</td>
</tr>
</tbody>
</table>

Tab. 4-6: EC and δ¹⁸O end-member values as applied for the different events. For events with more than 1 value the min-max range is displayed.

<table>
<thead>
<tr>
<th>EC (µScm⁻¹)</th>
<th>δ¹⁸O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater</td>
<td>-14.6</td>
</tr>
<tr>
<td>Rain</td>
<td>7.9</td>
</tr>
<tr>
<td>Rain</td>
<td>8.7</td>
</tr>
<tr>
<td>Rain</td>
<td>8.9</td>
</tr>
<tr>
<td>Glacier melt</td>
<td></td>
</tr>
<tr>
<td>Approach A</td>
<td>2.7</td>
</tr>
<tr>
<td>Approach B</td>
<td>3.0</td>
</tr>
<tr>
<td>Approach C</td>
<td>-</td>
</tr>
<tr>
<td>Approach D</td>
<td>2.4</td>
</tr>
</tbody>
</table>
Paper 2: Spatio-temporal tracer variability in the glacier melt end-member—How does it affect hydrograph separation results?
5 Paper 3: ‘Teflon basin’ or not? A high-elevation catchment transit time modelling approach

Jan Schmieder, Stefan Seeger, Markus Weiler and Ulrich Strasser

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My contribution to this article: field work, model code development, performing simulation, calculating young water fraction, producing plots, analysing results, and writing article.

Abstract

We determined the streamflow transit time and the subsurface water storage volume in the glacierized high-elevation catchment of the Rofenache (Oetztal Alps, Austria) with the lumped parameter transit time model TRANSEP. Therefore we enhanced the surface energy-balance model ESCIMO to simulate the ice melt, snowmelt and rain input to the catchment and associated δ¹⁸O values for 100 m elevation bands. We then optimized TRANSEP with streamflow volume and δ¹⁸O for a four-year period with input data from the modified version of ESCIMO at a daily resolution. The median of the 100 best TRANSEP runs revealed a catchment mean transit time of 9.5 years and a mobile storage of 13,846 mm. The interquartile ranges of the best 100 runs were large for both, the mean transit time (8.2–10.5 years) and the mobile storage (11,975–15,382 mm). The young water fraction estimated with the sinusoidal amplitude ratio of input and output δ¹⁸O values and delayed input of snow and ice melt was 47%. Our results indicate that streamflow is dominated by the release of water younger than 56 days. However, tracers also revealed a large water volume in the subsurface with a long transit time resulting to a strongly delayed exchange with streamflow and hence also to a certain portion of relatively old water: The median of the best 100 TRANSEP runs for streamflow fraction older than five years is 28%.
5.1 Introduction

High-elevation catchments were often seen as 'Teflon'-like basins (Williams et al., 2015), meaning that water input to the catchment immediately runs off as overland flow or fast subsurface flow with very limited subsurface interaction (Frenierre and Mark, 2014) and minimal infiltration, due to the permeability of bedrock typically assumed to be negligible (Frisbee et al., 2017). The concept of how catchments retain water is becoming almost equally recognized as how catchments release water (Buttle, 2016; McNamara et al., 2011; Spence, 2010; Staudinger et al., 2017). However, very recent studies mentioned the formerly unrecognized subsurface storage potential of mountain catchments (Cochand et al., 2019; Staudinger et al., 2017; Stoelzle et al., 2019), i.e., water is not only temporarily stored as snow and ice, but also in the soil, fractured bedrock, moraines, talus, alluvium, alluvial fans, permafrost, rock glaciers and rock slides (Hood and Hayashi, 2015; Jasechko et al., 2016; Käser and Hunkeler, 2016; Schmieder et al., 2018a; Staudinger et al., 2017). This water contributes to streamflow by shallow to deep flow paths (Frisbee et al., 2011; Frisbee et al., 2017), both in periods with rain, snowmelt and ice melt input and in periods without water input to the catchment (i.e., when the catchment is in a frozen state (Stoelzle et al., 2019)), and hence is an important contributor to streamflow. This subsurface water may play an important role in the alpine hydrologic cycle as shown by numerous studies in glacier-free and glacierized catchments (Andermann et al., 2012; Clow et al., 2003; Engel et al., 2016; Harrington et al., 2018; Hood and Hayashi, 2015; Liu et al., 2004; Penna et al., 2017). Snowmelt, ice melt and rain recharge the subsurface storage, with snowmelt being the most important contributor in many mountain catchments worldwide (Berghuijs et al., 2014; Musselman et al., 2017). The water volume and flow (the quotient is the transit time) thereby affect both, downstream water supply and quality (McGuire and McDonnell, 2006; Staudinger et al., 2017).

Streamflow age is a crucial descriptor of catchment functioning, affecting the control of runoff generation, biogeochemical cycling and contaminant transport. It is defined as the elapsed time for water transmitted through the catchment from input to the stream at the outlet (McDonnell et al., 2010; McGuire and McDonnell, 2006). The transit time distribution (TTD) describes the age composition of a streamflow water sample, and can be inferred from seasonal tracer cycles with the convolution integral method by relating past tracer input (e.g., precipitation) to tracer output (e.g., streamflow) (McGuire and McDonnell, 2006). The mean transit time (MTT) thereby describes the average travel time for a water parcel from entering to leaving a catchment (McGuire and McDonnell, 2006). Dynamic storage controls streamflow dynamics (i.e., the runoff response), whereas mobile storage, also connected to streamflow, shows large differences in water age and controls transport in a catchment (i.e., the tracer response) (Staudinger et al., 2017). An overview of perceptual storage terms in catchment hydrology and respective estimation methods can be found in Staudinger et al. (2017). The young water fraction (Fyw) is the proportion of streamflow below a certain threshold age (typically less than 3 months) and can be estimated by comparing fitted seasonal sine wave tracer cycles of catchment input and output (Kirchner, 2016a, b).
Streamflow age (including $F_{yw}$) and subsurface storage studies were already conducted in catchments in a variety of environmental settings: in low mountain catchments, e.g., (Stockinger et al., 2016; Stockinger et al., 2019), in northern high-latitude catchments, e.g., (Tetzlaff et al., 2014; Tetzlaff et al., 2018), in high mountain catchments, whereby only a few were covered by a small percentage of glacier ice (<5 %), e.g., (Seeger and Weiler, 2014; Staudinger et al., 2017; von Freyberg et al., 2018), or in permafrost regions, e.g., (Song et al., 2017). Seeger and Weiler (2014) combined a surface energy-balance model with a lumped parameter transit time model and reported MTTs of 0.6 to 10.5 years for five snow-dominated catchments in Switzerland. Staudinger et al. (2017) revealed dynamic and mobile storages of approximately 100 to 500 mm and 1000 to 13,000 mm for four snow-dominated catchments in Switzerland (these were included in the analyses of Seeger and Weiler, 2014), respectively. Freyberg et al. (2018) estimated a flow-weighted $F_{yw}$ of 0.1 to 0.22 for the same Swiss catchments analyzed in Seeger and Weiler (2014). A global study of 254 river systems revealed a flow-weighted mean $F_{yw}$ of 0.34 with a threshold age of 2.3 ± 0.8 months, whereas almost all of the mountain rivers had a lower $F_{yw}$ than the mean (Jasechko et al., 2016). Freyberg et al. (2018) tested the delayed effect of snowmelt during their application of the $F_{yw}$ approach and found a significant difference in the amplitude of fitted seasonal tracer cycle of input water for only one out of 21 catchments compared to the method with a direct input of precipitation. They concluded that in their study catchments, $F_{yw}$ values were not sensitive to the use of delayed input. Tetzlaff et al. (2018) extended the traditional transit time estimation approach with a snow model that provides snow melt volume and isotope ratio and applied it in an Arctic catchment. They concluded that considering all available inflows (i.e., snow melt, soil ice thaw and rainfall) led to the best estimated transit time. Hence we hypothesize that the spatio-temporal variability of the water input in glacierized high-elevation catchments (i.e., especially the snow and ice melt volume and their isotope ratios) is important, which challenges the traditional transit time and $F_{yw}$ approach (where rain is considered to contribute dominantly).

It can be concluded that studies addressing the $F_{yw}$, catchment TTD or storage estimates in catchments with >5 % glacierized area are missing and estimates of the above-mentioned metrics are unknown, but high-elevation catchment storage (not snow and ice) may become even more important in terms of a changing climate and shrinking glaciers. The question arises how the occurrence of ice melt as a contributor and significant part of the water cycle affects the estimation of $F_{yw}$, catchment TTD and storage in glacierized high-elevation catchments. We make use of a model coupling approach in which we combine a surface energy-balance model to simulate the snow and ice melt volume and isotope ratio with a lumped parameter transit time model to estimate the catchment TTD and storage. Overall, we aim to identify the role of subsurface water (and storage) in a glacierized high-elevation catchment with the use of $\delta^{18}$O. Specifically, the objectives are:

1. The estimation of catchment transit time and mobile storage by coupling of a surface energy-balance snow and ice melt model with a lumped parameter transit time model,
2. the estimation of the $F_{yw}$ with delayed input of snow and ice melt using the sine wave approach and,
(3) the comparison of the TTD and the $F_{\text{eq}}$.

5.2 Materials and methods

5.2.1 Study area

We conducted our study in the 35% glacierized high-elevation catchment Rofental (Fig. 5-1), a LTSER site in the Austrian Alps (https://www.lter-austria.at/rofental/). The catchment (98 km$^2$) ranges from approximately 1890 to 3770 m a.s.l. (mean elevation is 2930 m a.s.l.). The Rofenache is draining the catchment and has a distinct glacial regime with a mean flow of 4.6 m$^3$/s$^{-1}$ (1971–2013) at the outlet in Vent (1891 m a.s.l., 46.85722 °N, 10.91083 °E). Mean 7-day annual minimum flow, mean flow and mean annual peak flow for the period 2014 to 2017 are 0.43, 3.93 and 24.59 mm d$^{-1}$, respectively.

Detailed site descriptions, including various climatic and hydrologic characteristics, can be found in Schmieder et al. (2016) or in Strasser et al. (2018). Several cryospheric, hydrologic and geodetic studies have been conducted in the catchment and data sets from more than 150 years ago up to very recently are freely available (Strasser et al., 2018). Hydrologic tracer studies have been conducted intensively during the International Hydrological Decade (1965–1974) (Keller, 1976) and since 2014 (Schmieder et al., 2018b). Strasser et al. (2018) provide a detailed overview about the research history in the Rofental. Fig. 5-1 shows the catchment, as well as the water sampling and ‘Austrian Network of Isotopes in Precipitation and Surface Waters’ (ANIP) sites used in this publication.
5.2.2 Data

We used daily runoff data (streamflow was measured at the gauging station in Vent) within this study. Hourly meteorological variables (air temperature, precipitation amount, relative humidity, wind speed and global radiation) were measured at various stations (see Hanzer et al. (2016, 2018) for more details) and were interpolated with the hydroclimatological modeling system AMUNDSEN (Hanzet al. 2016; Strasser, 2008) to 50 m pixel resolution grids. For further model input in this study, these grids were aggregated to 100 m elevation bands ($n = 19$) in daily resolution.

Streamflow isotope samples ($n = 98$) were collected in non-equitemporal intervals for 2014 to 2016 (grab samples) and in daily intervals for 2017 (automatic water sampler) at the gauging station at Vent. The water samples were mostly collected during daytime in the ablation season. For days with multiple samples a flow-weighted mean was calculated. The sampling time is documented in Tab. 5-5.

Monthly long-term precipitation isotope data of the surrounding ANIP stations (Fig. 5-1) were used to calculate monthly lapse rates of $\delta^{18}O$. These lapse rates were applied to the ANIP station in Obergurgl (1942 m a.s.l., 46.866667° N, 11.024444° E, see Fig. 5-1) to regionalize the $\delta^{18}O$ of precipitation registered there (100 m elevation bands). The Obergurgl $\delta^{18}O$ values of precipitation were assumed to be transferable to the catchment since regression of precipitation $\delta^2H$ values from Vent and Obergurgl revealed a very high correlation ($R^2 = 0.89$) for the years 1972 to 1975 (Maier, 2017). Lapse rate data (Tab. 5-3 and Tab. 5-4) and the regression plot (Fig. 5-6) can be found in the supplement.

Snowmelt isotopic data was not derived from sampling, but was modeled from precipitation isotopic data (as described in Chapter 5.2.3). Supraglacial meltwater (hereafter ice melt) was sampled on Hochjochferner ($n = 72$) at an elevation of approximately 2700 m a.s.l. at various temporal (including sub-daily and month-to month) and spatial resolutions (spatial extent: 100s of meter). Samples have been collected when most of the glacier was snow-free.

The isotope data (not ANIP data) has been partially described already (Schmieder et al., 2018a; Schmieder et al., 2016; Schmieder et al., 2017; Schmieder et al., 2018b). Water samples were stored cold and dark before analyses with cavity ring-down spectroscopy (Picarro Inc., Santa Clara, California). The accuracy, indicated by the standard deviation of at least six repeated measurements, was ≤0.1 ‰. $^{18}O/{^{16}O}$ isotope ratios are reported as $\delta^{18}O$ (in ‰) relative to the Vienna standard mean ocean water (VSMOW). The modeling workflow is described in the following sections and a schematic overview is displayed in Fig. 5-7.

5.2.3 The surface energy-balance model ESCIMO

We used the modified version (Seeger and Weiler, 2014) of the surface energy-balance model ESCIMO (Strasser and Marke, 2010) to simulate the rain, snow and ice melt input fluxes and the respective $\delta^{18}O$ values for 100 m elevation bands. ESCIMO has been successfully applied at low and high mountain sites, e.g., (Krinner et al., 2018; Marke et al., 2016). A similar setup like in our study has been already applied successfully (Seeger and Weiler, 2014; Staudinger et al., 2017; von Freyberg et al., 2018), where snow melt $\delta^{18}O$ was simulated as the weighted average of individual snowfall events without addressing isotopic fractionation explicitly. $\delta^{18}O$
of ice melt was not considered in those studies since the glacierized area of the test catchments was <5%. ESCIMO inputs are meteorological variables as described in Chapter 5.2.2 and δ¹⁸O in precipitation. We enhanced ESCIMO to simulate ice melt volumes. Therefore ESCIMO is enabled to calculate melt rates when snow water equivalent is zero. Potential ice melt rates are then multiplied with the glacierized fraction of the respective elevation band to calculate semi-distributed ice melt input fluxes. We ascribed the simulated ice melt volume in each elevation band a δ¹⁸O value to account for spatial variability as done in similar studies, e.g., (He et al., 2019). This value is the median of the measured ice melt δ¹⁸O values at the elevation of 2700 m a.s.l. (−15.4‰) and changes according to the mean lapse rate (−0.221‰/100 m) of δ¹⁸O in precipitation between November and May (as described in Chapter 5.2.2). The temporal variability of δ¹⁸O in ice melt was not considered.

5.2.4 The lumped parameter transit time model TRANSEP
The lumped parameter transit time model TRANSEP (Weiler et al., 2003) was used to estimate the time-invariant TTD and response time distribution (RTD), as well as the dynamic and mobile storage. TRANSEP has been applied successfully in catchments with various environmental conditions, e.g., (Roa-García and Weiler, 2010; Segura et al., 2012; Stockinger et al., 2016), and also in high mountain catchments, e.g., Seeger and Weiler (2014). ESCIMO output data (i.e., catchment water input Pₑ: the sum of rain, snow and ice melt volumes; Cₑ: the amount-weighted δ¹⁸O value of rain, snow and ice melt) were spatially aggregated to the catchment scale and used as input data for TRANSEP. The model was run at a daily resolution.

TRANSEP simulates discharge for each time step t with Eq. 5-1, where \( g(\tau_R) \) is the transfer function for discharge (Eq. 5-2) with \( \tau_R, \varphi, \tau_f \) and \( \tau_s \) being the response time, fraction of fast reservoir and the MTT of the fast and the slow reservoir, respectively. Eq. 5-2 is calibrated with measured streamflow data.

\[
Q(t) = \int_0^t g(\tau_R) P_R(t - \tau_R) d\tau_R \tag{5-1}
\]

\[
g(\tau_R) = \Phi \frac{\tau_R}{\tau_f} \exp\left(-\frac{\tau_R}{\tau_f}\right) + \frac{1-\Phi}{\tau_s} \exp\left(-\frac{\tau_R}{\tau_s}\right) \tag{5-2}
\]

δ¹⁸O values of streamflow are simulated with Eq. 5-3, where \( h(\tau_T) \) is the transfer function for streamflow δ¹⁸O (Eq. 5-4), with \( \tau_T \) being the transit time, and \( \alpha \) and \( \beta \) being the shape and scale parameter, respectively. Eq. 5-4 is calibrated with measured streamflow δ¹⁸O.
After initial testing, we chose the two parallel linear reservoirs (TPLR) for the discharge transfer function (i.e., Eq. 5-2) and the gamma distribution (GM) for the tracer transfer function (i.e., Eq. 5-4). These gave the best results with respect to the objective function.

To optimize the simulated discharge, we used a scaled variant (Mizukami et al., 2019) of the Kling-Gupta efficiency (KGE) (Kling et al., 2012). It emphasizes the flow variability term ($\alpha$): A two times higher weight compared to the bias ($\beta$) and the correlation term ($r$) was used. Therefore we maximized $\text{KGE}_Q$ (Eq. 5-5) for the period 2014 to 2017.

$$\text{KGE}_Q = 1 - \sqrt{[1(r-1)]^2 + [2(a-1)]^2 + [1(\beta-1)]^2}$$

(5-5)

We optimized the simulated $\delta^{18}O$ in streamflow by minimizing $\text{OF}_C$ (Eq. 5-6), using the KGE (with the same weighting as used for optimizing discharge). We split the time series into two periods according to the temporal sampling intervals (as described in Chapter 5.2.2): 1) low frequency period (lf) 2014–2016 and 2) high-frequency period (hf) 2017. For a simpler readability we reported the KGE with standard scaling hereafter.

$$\text{OF}_C = 0.75(1 - \text{KGE}_{lf}) + 0.25(1 - \text{KGE}_{hf})$$

(5-6)

For the optimization procedure we used a Monte Carlo simulation with 10,000 runs and uniformly distributed parameters. The initial parameter ranges for Eq. 5-2 and Eq. 5-4 were $\varphi$ [0.1,0.9], $\tau_f$ [0.5,15], $\tau_s$ [20,600], $\alpha$ [0.01,1] and $\beta$ [1·10^{-8},3·10^{-4}]. The best 1% of the runs ($n = 100$), with the highest value of $\text{KGE}_Q$ (Eq. 5-5) and the lowest value of $\text{OF}_C$ (Eq. 5-6) were considered for further analyses. The mean response time (MRT) and MTT were calculated with Eq. 5-7 and Eq. 5-8.

$$\text{MRT} = \phi \tau_f + (1 - \phi) \tau_s$$

(5-7)

$$\text{MTT} = \alpha \beta$$

(5-8)

Dynamic and mobile storage has been calculated by multiplying mean flow with the MRT and the MTT, respectively. Tab. 5-5 includes the observed runoff and $\delta^{18}O$ value of streamflow, as well as the catchment water input and its respective $\delta^{18}O$ value as modeled with ESCIMO.

### 5.2.5 Estimating the young water fraction with the sine wave approach

We calculated the $F_{yw}$ following Kirchner (2016a) and Stockinger et al. (2016). First, seasonal $\delta^{18}O$ cycles in input water and streamflow (Eq. 5-9 and Eq. 5-10) were fitted by multiple linear
regression with an iteratively reweighted least squares algorithm (provided by Freyberg et al., 2018). $C_E$ and $C_S$ are the $\delta^{18}O$ values of input water as modeled with ESCIMO and measured streamflow at time $t$, and were weighted with $P_E$ and observed runoff, respectively. $a_E$, $b_E$, $k_E$, $a_S$, $b_S$ and $k_S$ are the cosine and sine coefficient parameter and the vertical shift for input water and streamflow, respectively. $f$ is the frequency ($1/365.25$).

\[
C_E(t) = a_E \cos(2\pi ft) + b_E \sin(2\pi ft) + k_E 
\] (5-9)

\[
C_S(t) = a_S \cos(2\pi ft) + b_S \sin(2\pi ft) + k_S 
\] (5-10)

The amplitudes ($A$) of the seasonal $\delta^{18}O$ cycles of input water and streamflow (Eq. 5-11 and Eq. 5-12) are calculated as:

\[
A_E = \sqrt{a_E^2 + b_E^2} 
\] (5-11)

\[
A_S = \sqrt{a_S^2 + b_S^2} 
\] (5-12)

and the phases $\varphi_E$ and $\varphi_S$ (in rad) are calculated as:

\[
\varphi_E = \tan^{-1}\left(\frac{b_E}{a_E}\right) 
\] (5-13)

\[
\varphi_S = \tan^{-1}\left(\frac{b_S}{a_S}\right) 
\] (5-14)

We iteratively solved Eq. 5-15 to calculate the shape parameter $\alpha$ of a gamma distribution.

\[
\varphi_S - \varphi_E = \alpha \tan^{-1}\left(\sqrt{(A_S/A_E)^{-2/\alpha} - 1}\right) 
\] (5-15)

The scale parameter $\beta$ (Eq. 5-16) was calculated as:

\[
\beta = \frac{1}{2\pi f} \sqrt{(A_S/A_E)^{-2/\alpha} - 1} 
\] (5-16)

By solving Eq. 5-17 we calculated the threshold age $\tau_{yw}$ that defines $F_{yw}$ with water younger than this value. $F_{yw}$ is calculated with Eq. 5-18 using the lower incomplete gamma function $\Gamma(\tau_{yw},\alpha,\beta)$. 

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\[ \tau_{yw} = 0.0949 + 0.1065 \alpha - 0.0126 \alpha^2 \]  
\[ F_{yw} = \Gamma(\tau_{yw}, \alpha, \beta) = \int_{\tau=0}^{\tau_{yw}} \frac{\tau^{\alpha-1}}{\beta \Gamma(\alpha)} e^{-\tau/\beta} d\tau \]  

We call this F\(_{yw}\) estimation approach ‘delayed daily F\(_{yw}\)’ since it accounts for the delayed contribution of snow and ice melt as simulated with ESCIMO. We also calculated the non-delayed monthly F\(_{yw}\) and the delayed monthly F\(_{yw}\) for comparison reasons. For the non-delayed monthly F\(_{yw}\) we used the input precipitation data as used for the ESCIMO simulation (see in Chapter 5.2.2) and aggregated it to the monthly resolution (because the ANIP data used for the isotope interpolation is in monthly resolution). This approach does neither account for any temporal storage as snow and ice, nor the delayed release from snow and ice. Since resolution may play a role in estimating the F\(_{yw}\) (Stockinger et al., 2016), we also estimated the delayed monthly F\(_{yw}\) to compare the results related to the effect of the delayed and the non-delayed input (both then at the same temporal resolution). For the delayed monthly F\(_{yw}\) we simply aggregated P\(_E\) (sum) and C\(_E\) (volume-weighted average) and performed the analyses in monthly resolution.

We calculated the uncertainty in all three F\(_{yw}\) approaches by fitting each sine wave 10,000 times. For this, we used randomly sampled sine and cosine coefficient parameter (a and b in Eq. 5-9 and Eq. 5-10) out of a normal distribution with the mean being the respective parameter as estimated with Eq. 5-9 to Eq. 5-18, and a standard deviation equal to the standard error of the multiple linear regression analyses. Fit statistics, as well as regression parameter and their standard errors can be found in Tab. 5-6.

5.3 Results

5.3.1 \(\delta^{18}O\) values of various water types in the Rofental for the period 2014 to 2017

Fig. 5-2 shows boxplots of the \(\delta^{18}O\) values in rain, snow melt, ice melt and streamflow for the period 2014 to 2017. Rain and snow melt \(\delta^{18}O\) values were simulated with ESCIMO (catchment scale). The boxplots reveal a high temporal variability in both, rain and snow melt, with snow melt having a markedly lower median (−15.6 \(\%\)) than rain (−11.4 \(\%\)). Rain \(\delta^{18}O\) values were significantly different from snowmelt, ice melt and streamflow \(\delta^{18}O\) (Kruskal-Wallis test: \(p < 0.001\)). The ice melt boxplot represents the time-invariant values of each elevation band derived from measured \(\delta^{18}O\) values and interpolated as described in Chapter 5.2.2 and hence displays the spatial variability in Fig. 5-2. The median (−15.4 \(\%\)) was slightly higher and the interquartile range is damped compared to snowmelt. Streamflow represents the measured data (temporal variability) as used for the optimization of TRANSEP, had a median of −14.9 \(\%\) and was damped compared to the rain and snow melt input.
5.3.2 Flux and δ18O of water input into the Rofenache catchment

Monthly isotopic lapse rates were estimated using surrounding long-term data from ANIP stations. $R^2$ for monthly δ18O-elevation relationships ranged from 0.46 to 0.94 (Tab. 5-4). The lapse rates showed seasonality with steeper gradients in winter (March: $-0.265$ ‰/100 m) and flatter gradients in summer (July: $-0.112$ ‰/100 m). Further information is provided in the supplement (Tab. 5-3 and Tab. 5-4).

The interpolated precipitation input (non-delayed) into the catchment (black line in Fig. 5-3a), i.e., the sum of snowfall and rain, reveals a slight seasonal cycle with values of about 100 mm month$^{-1}$. The delayed liquid water input into the catchment (light blue line in Fig. 5-3a), i.e., the sum of rain, snow and ice melt modeled with ESCIMO, had a strong seasonal characteristic with close to or zero input during the winter months (December to March) and very high inputs $>350$ mm month$^{-1}$ during the peak ablation period (June to August).
Fig. 5-3: (a) Monthly water input into the catchment, and (b) its respective $\delta^{18}O$ value during the period 2014 to 2017. The non-delayed input represents precipitation, i.e., the sum of snow and rainfall, and the delayed input is the sum of rain, snow and ice melt as modeled by ESCIMO. The delayed input is aggregated to monthly resolution to make both approaches comparable (description in Chapter 5.2.5), i.e., the monthly sum $P_E$ (a) and the volume-weighted monthly mean $C_E$ (b).

The $\delta^{18}O$ value of catchment input shows a strong seasonality for both, the delayed ESCIMO catchment input ($P_E$) and the interpolated non-delayed precipitation catchment input (light blue and black lines in Fig. 5-3b). The delayed monthly $\delta^{18}O$ values ($C_E$) ranged from $-18.7$ ‰ to $-10.2$ ‰ and exhibited more damped amplitude than the non-delayed $\delta^{18}O$ values ($-22.0$ ‰ to $-5.5$ ‰).

5.3.3 Runoff and $\delta^{18}O$ in streamflow of the Rofenache at the gauging station in Vent

Fig. 5-4a shows the observed and simulated (with TRANSEP) daily runoff for the period 2014 to 2017 for the gauging station in Vent (1891 m a.s.l.). Mean 7-day annual minimum flow, mean flow and mean annual peak flow of the simulation runs (median of best 100 runs) were 0.46, 3.79 and 21.47 mm d$^{-1}$, respectively. Both, observed and simulated runoff show a very strong seasonality, with high flows and high day-to-day variability during the ablation period (>10 mm d$^{-1}$ from June to August) and low flows concomitant with low day-to-day variability during the winter baseflow period (<1 mm d$^{-1}$ from December to March). The KGE for runoff (best 100 runs) was 0.97.
Observed and simulated streamflow $\delta^{18}O$ (median of best 100 runs) also reveal a strong seasonality with the highest values during late summer and the lowest values during the peak snowmelt period in late spring (Fig. 5-4b). The simulated $\delta^{18}O$ values ranged from $-17.6 \%$ to $-7.8 \%$ with respect to the best 100 TRANSEP simulations (the orange band in Fig. 5-4b is very thin and covered by the orange line). The range of the 98 observed streamflow $\delta^{18}O$ values was $-16.9 \%$ to $-12.5 \%$. During winter baseflow conditions (December to March), the simulated $\delta^{18}O$ values with a range of $-15.3 \%$ to $-13.4 \%$ (median of the best 100 TRANSEP runs) were close to the median of the observed ones for the whole period ($-14.9 \%$) and reflected a small day-to-day variability (similar to the observed values during the baseflow period). The KGE for streamflow $\delta^{18}O$ (best 100 runs) ranged between 0.84 and 0.86.

### 5.3.4 Streamflow water age and subsurface storage

#### Young water fraction estimated with the sine wave approach

We fitted sine waves to the input and output data with an iteratively reweighted least squares algorithm for calculating $F_{yw}$ using three different input characterizations, i.e., the delayed daily, the delayed monthly, and the non-delayed monthly input (cf. Chapter 5.2.5). The $p$ values were below 0.1 for all regression coefficients of Eq. 5-9 and Eq. 5-10, except for $a_{E}$ when fitting the delayed monthly input. $R^2$ was 0.38, 0.58, 0.82 and 0.71 for the fits of the
delayed daily, delayed monthly and non-delayed monthly input and streamflow, respectively (Tab. 5-6). The delayed daily $F_{yw}$ was 0.47 with an interquartile range of 0.45 to 0.50 and the delayed monthly $F_{yw}$ and the non-delayed monthly $F_{yw}$ were 0.54 (0.47–0.60) and 0.28 (0.26–0.30), respectively (Tab. 5-1). The young water threshold ages ($\tau_{yw}$) were 56, 44 and 67 days for the delayed daily, delayed monthly and non-delayed monthly $F_{yw}$, respectively. The phase shift ($\phi_S - \phi_E$) was largest for the non-delayed monthly $F_{yw}$ (1.24 rad), followed by the delayed daily (0.76 rad) and delayed monthly $F_{yw}$ (0.37 rad). The iterative solution of the algorithm (Eq. 5-15) did not work for each of the 10,000 runs when applied for the delayed monthly $F_{yw}$, likely due to negative values of $\phi_S - \phi_E$ (i.e., streamflow runs off before water input), which may have resulted from the high $p$ value and large standard error of $a_E$ (Tab. 5-6). Hence we calculated the interquartile range of the delayed monthly $F_{yw}$ by using the ratio $A_S/A_E$ and were not able to calculate the interquartile range for $\alpha$ and $\tau_{yw}$ (see Tab. 5-1). The shape parameter $\alpha$ for the three approaches ranges from 0.25 to 0.93. Tab. 5-1 lists the described metrics and their interquartile ranges.

<table>
<thead>
<tr>
<th>Method</th>
<th>$A_E$ (%)</th>
<th>$A_s$ (%)</th>
<th>$\tau_{yw}$ (d)</th>
<th>$\alpha$ (–)</th>
<th>$\phi_S - \phi_E$ (rad)</th>
<th>$F_{yw}$ (–)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delayed daily input</td>
<td>3.1 (3.01-3.2)</td>
<td>1.44 (1.37-1.54)</td>
<td>56 (52-60)</td>
<td>0.59 (0.47-0.72)</td>
<td>0.76 (0.65-0.87)</td>
<td>0.47 (0.45-0.5)</td>
</tr>
<tr>
<td>Delayed monthly input</td>
<td>2.69 (2.48-3.07)</td>
<td>1.44 (1.36-1.55)</td>
<td>44 (NA)</td>
<td>0.25 (NA)</td>
<td>0.37 (0.18-0.54)</td>
<td>0.54 (0.47-0.6)</td>
</tr>
<tr>
<td>Non-delayed monthly input</td>
<td>5.43 (5.22-5.66)</td>
<td>1.44 (1.37-1.55)</td>
<td>67 (63-71)</td>
<td>0.93 (0.8-1.07)</td>
<td>1.24 (1.11-1.36)</td>
<td>0.28 (0.26-0.3)</td>
</tr>
</tbody>
</table>

**Age distribution and subsurface storage potential**

Fig. 5-5 shows the cumulated RTD and TTD using the convolution integral method (TRANSEP), as well as the gamma distribution derived during the delayed daily $F_{yw}$ approach (sine wave approach). The delayed daily $F_{yw}$ had a narrow band (interquartile range of 10,000 runs), as well as the RTD and TTD estimated with TRANSEP (interquartile range of best 100 runs). The cumulated TRANSEP TTD at the threshold age of 56 days ranged between 0.43 and 0.45 (25th–75th percentile) with a median of 0.44 for the best 100 runs (Tab. 5-2). Tab. 5-2 reveals the transfer function parameters for the TPLR and the GM. Median (interquartile range) MRT and MTT were 0.13 (0.08 to 0.19) and 9.5 (8.2–10.5) years, respectively. The median of the cumulated TTD at the threshold age of 5 years ($F_{ow}$) was 0.28 (i.e., 28% of water was older than 5 years). The median (interquartile range) of the dynamic and mobile storages estimated with TRANSEP was 195 (110–284) mm and 13,846 (11975–15382) mm, respectively.
Fig. 5-5: Cumulated response time distribution (RTD; yellow) and transit time distribution (TTD; green) estimated with TRANSEP, as well as delayed daily $F_{yw}$ estimated with the sine wave approach (grey). The bands indicate the interquartile range of the best 100 runs for the RTD and the TTD, and the interquartile range of the 10,000 $F_{yw}$ calculations. The dashed line marks the threshold age $\tau_{yw}$ of 56 d.

Tab. 5-2: Medians and interquartile ranges of two parallel linear reservoirs (TPLR) and gamma distribution (GM) parameters of best 100 TRANSEP runs.

<table>
<thead>
<tr>
<th>Metric</th>
<th>25th percentile</th>
<th>50th percentile</th>
<th>75th percentile</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$ [-]</td>
<td>0.14</td>
<td>0.14</td>
<td>0.15</td>
</tr>
<tr>
<td>$\beta$ (d)</td>
<td>20606</td>
<td>24451</td>
<td>27266</td>
</tr>
<tr>
<td>MTT (d)</td>
<td>2994</td>
<td>3462</td>
<td>3847</td>
</tr>
<tr>
<td>Mobile storage (mm)</td>
<td>11975</td>
<td>13846</td>
<td>15382</td>
</tr>
<tr>
<td>$\tau_f$ (d)</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>$\tau_s$ (d)</td>
<td>117</td>
<td>263</td>
<td>435</td>
</tr>
<tr>
<td>$\Phi$ (-)</td>
<td>0.76</td>
<td>0.81</td>
<td>0.84</td>
</tr>
<tr>
<td>MRT (d)</td>
<td>28</td>
<td>49</td>
<td>71</td>
</tr>
<tr>
<td>Dynamic storage (mm)</td>
<td>110</td>
<td>195</td>
<td>284</td>
</tr>
<tr>
<td>$F_{yw}$ (-)</td>
<td>0.43</td>
<td>0.44</td>
<td>0.45</td>
</tr>
<tr>
<td>$F_{ow}$ (-)</td>
<td>0.26</td>
<td>0.28</td>
<td>0.29</td>
</tr>
</tbody>
</table>

5.4 Discussion

5.4.1 How large is the subsurface storage potential?
Using TRANSEP, we found a relatively large dynamic (195 mm) and a very large mobile storage (13,846 mm), which were, though, in the range of values reported for other high-mountain catchments (up to 13,000 mm; see Chapter 5.1; e.g., Seeger and Weiler, 2014 and
Stuadinger et al., 2017). Overburden material (such as glacial deposits, talus or alluvium) and soil/bedrock may serve as a physical storage for this water. Since subsurface information from wells or boreholes were not available we could not yet evaluate this hypothesis, but overburden material covers a high percentage of the catchment (42%, Schmieder et al., 2016) and is assumed to be many meters deep in some parts of the catchment (Klug et al., 2017). Soil is usually <1 m thin, providing a relatively limited storage potential, hence bedrock is attributed to store and transmit larger portions of water, most likely in fractures. The bedrock storage might be obvious due to the large elevation difference of almost 2000 m from the highest peak to the catchment outlet, indicating a large volume of material, which provides potential storage (McGuire et al., 2005). The total catchment water storage (not snow and ice) hence provides a huge tank for tracer mixing. The large range in dynamic and mobile storage in the TRANSEP results (Tab. 5-2) indicates a high uncertainty, as known also for other transit time models (e.g., McHuire and McDonnell, 2006). This uncertainty is triggered by the high variability of the parameter \( \tau_s \) and \( \beta \) (Tab. 5-2), which were not well-constrained during the calibration procedure (see Chapter 5.4.3).

5.4.2 How old is streamflow?

Contrary to the large storage volumes estimated with TRANSEP, we also found a high \( F_{yw} \) of 0.47 as estimated with the sine wave approach. Our estimate was markedly higher than the flow-weighted mean of 254 catchments (0.34) in Jasechko et al. (2016), or estimates from other high-elevation catchments (e.g., maximum flow-weighted \( F_{yw} \) was 0.22 von Freyberg et al., 2018). This can be attributed to mainly two effects. Firstly, we used the delayed input of snow and ice melt simulated with ESCIMO. This flattened out the seasonal cycle of \( \delta^{18}O \) (see Fig. 5-3 and parameter \( A_k \) in Tab. 5-1). The non-delayed \( F_{yw} \) of 0.28 was much smaller and closer to the other values reported in the literature. Secondly, and related to the first effect, snow and ice melt had a disproportional high impact on runoff and streamflow \( \delta^{18}O \) because snow and ice melt input volumes were relatively large and relatively fast transmitted (especially large portions of ice melt) to the stream network during a limited period of the hydrological year (i.e., the ablation period). Up to now, there are no studies available that address this topic, but we thought this was intuitively plausible and should be investigated in future studies with more detail.

Interestingly, we also found a marked \( F_{ow} \): 28% of streamflow water was considered to be older than five years. TRANSEP \( F_{yw} \) was 0.44, so the resulting concomitant occurrence of high fractions of younger and older water in streamflow might be a combination of two facts: 1) the high \( F_{yw} \) triggered by the fast transmittal of ice and snow melt as outlined above and 2) the high \( F_{ow} \) provided by the large storage described in Chapter 5.4.1. Longer transit times (>5 years) are seen as critical when applying the convolution integral method with stable isotopes (Stewart et al., 2007; Stewart et al., 2010; Stewart et al., 2012), but method restrictions were discussed in Chapter 5.4.3.

The estimated MTT of 9.5 years was potentially biased, as recently postulated by Kirchner (2016a and b). Although it is known that ”stable isotopes are effectively blind to the long tails of transit time distributions” (Kirchner, 2016a), we still used \( \delta^{18}O \) (as also suggested by Seeger
and Weiler, 2014), since no other tracers (e.g., $^3$H) were available. Our estimate was at the top end compared to MTTs (0.6–10.5 years) of other snow-melt dominated high-elevation catchments in Switzerland (Seeger and Weiler, 2014). Behrens (1978) estimated the winter baseflow MTT (4 years) for the period 1972 to 1975 at approximately four years for the same catchment, but they used a different tracer ($^3$H), a different transfer function (exponential model), non-delayed input and they focused on winter baseflow transit time (low flow regime). Unfortunately, any other direct comparison to other glacierized catchments was still lacking.

5.4.3 Methodological implications

Modelling catchment water input and its $\delta^{18}$O value with ESCIMO

Using monthly $\delta^{18}$O values in precipitation to simulate daily $\delta^{18}$O water input values is a restriction and hinders the determination of highly variable $\delta^{18}$O values of rain and snowmelt, as frequently observed in empirical studies (e.g., Schmieder et al., 2016; McDonnell et al., 1990). Additionally, the use of the $\delta^{18}$O lapse rate in precipitation is a source of uncertainty, since local effects (e.g., windward vs. leeward) may not be reproduced by the regional pattern of the lapse rate. Still, our approach represents a stable approach in that it uses long-term data. Our lapse rates compared well to the lapse rate in Austria (−0.19 ‰/100 m) (Hager and Foelsche, 2015) and Switzerland (−0.27 ‰/100 m) (Beria et al., 2018). Due to the absence of high-frequency and high-density input $\delta^{18}$O data in our study area, we were bound to the design used in this study, but future work should include intense sampling and/or disaggregation methods.

Although we used $\delta^{18}$O ice melt data measured in the field to derive $\delta^{18}$O ice melt input data for ESCIMO, the spatio-temporal variability, as observed in empirical studies (Engel et al., 2019; Schmieder et al., 2018a; Zuecco et al., 2019), provides an alternative source of uncertainty. An isotopic lapse rate was not directly estimated from the ice melt samples, rather it was estimated from the mean winter precipitation lapse rate. We used temporally invariant $\delta^{18}$O values of ice melt due to missing temporally distributed data throughout the four-year period, but temporal variability has also not yet been described intensively (Engel et al., 2019; Schmieder et al., 2018a; Zuecco et al., 2019). Our estimate (−0.221 ‰/100 m) compared well to values presented in other studies; e.g., He et al. (2019) directly estimated an isotopic glacier melt lapse rate from $\delta^{18}$O measurements at −0.226 ‰ per 100 m in a 17 % glacierized high-elevation catchment in the Tien Shan and used it for their modeling study.

The resolution of ESCIMO (100 m elevation bands and one day) seems a reliable balance in terms of data availability and sufficient process representation. Recent studies used fully distributed approaches to model the $\delta^{18}$O snowmelt input into the catchment (Ala-aho et al., 2017b; Piovano et al., 2019; Tetzlaff et al., 2018), but the advantage of this more data-intensive approach over the semi-distributed one needs to be evaluated. It remains a critical topic how much detail is needed when considering that the distributed data is aggregated to the catchment scale for further input in simpler models, such as lumped parameter transit time models or for the calculation of $F_{yw}$ with the sine wave approach.
A shortcoming of ESCIMO is the missing implementation of isotopic fractionation during the transition from snowfall to snowmelt. We used the volume-weighted mean of snowfall as snowmelt $\delta^{18}O$ similar to Seeger and Weiler (2014). According to the hypothesis of Beria et al. (2018), the median of individual snowfall events is close to the median of outflowing snowmelt water over one season, which makes this approach plausible. On the other side, the short-term temporal variability (e.g., depleted signal during first melt impulse) is not directly incorporated, and the data-intensive accounting for isotopic fractionation due to top layer sublimation and percolation through the snowpack should be accounted for in detailed studies, as initially presented by Ala-aho et al. (2017a). Validation data, especially with appropriate temporal and spatial resolution ($\delta^{18}O$ and areal snowmelt) is often absent. In our study, liquid water input by ice and snow melt into the catchment seemed plausible and was comparable to the results of other studies in the catchment (Hanzer et al., 2016, 2018). Although the approach was comprised of some restrictions, mostly due to data availability, we still thought that considering snow and ice melt—at least at the semi-distributed scale—was mandatory when characterizing catchment water inputs for the further estimation of the $F_{yw}$ or as input in transit time models.

The young water fraction of a glacierized high-elevation catchment

We could not support the hypothesis of Jasechko et al. (2016) that mountain catchments have less young streamflow, since we found a higher $F_{yw}$ compared to most other mountain catchments (see Chapter 5.4.2). We attributed this result to the use of the delayed input, as outlined in Chapter 5.4.2, and the occurrence of high snow and ice melt contributions to streamflow with typical residence times of hours (glacier) to weeks (snowpack) (Ambach et al., 1974; Behrens et al., 1976), which might not have been included in the dataset of Jasechko et al. (2016). The delayed monthly $F_{yw}$ (0.54) was twice the non-delayed monthly $F_{yw}$ (0.28). In a pre-study, a mean $F_{yw}$ of 0.16 was estimated using non-delayed monthly precipitation $\delta^{18}O$ data from Vent for the periods 1972–1977 and 2015–2016 (Maier, 2017). Contrary to the marked differences we observed for our dataset when computing $F_{yw}$ with non-delayed input data (direct precipitation input) or delayed input data (unretained precipitation + snow/ice melt from ESCIMO), von Freyberg et al. (2018) found no significant difference between the results of the two ways to compute $F_{yw}$ for 22 Swiss catchments, likely due to the absence of marked ice melt inputs from glaciers, as they did not include glacierized catchments in their study.

The temporal resolution played a role when applying the $F_{yw}$ approach, since we estimated a seven percent higher $F_{yw}$ when estimating the delayed monthly $F_{yw}$ compared to the delayed daily $F_{yw}$, but the difference was not as large as the one presented by Stockinger et al. (2016), who estimated $F_{yw}$ with daily data as almost twice that of $F_{yw}$ when using weekly data.

Although all regression coefficient parameters of the delayed daily and the non-delayed monthly sine wave fits had $p$ values below 0.1, the delayed daily fit had a markedly lower variance explained ($R^2 = 0.38$) compared to the non-delayed fit ($R^2 = 0.82$). This may be due to the missing input volume during the winter months and the extreme high input volumes during the ablation period. Such variable input is a serious challenge for the volume-weighted
sine wave fit. Unfortunately, $F_w$ estimates from other highly glacierized catchments were absent for comparison and hence we call for future studies.

**TRANSEP applied in glacierized high-elevation catchment**

We estimated the catchment TTD (not baseflow TTD) with $\delta^{18}O$ in a highly glacierized catchment for the period 2014 to 2017. Therefore we used streamflow $\delta^{18}O$ samples collected during various flow regime periods, from winter baseflow to annual peak flow. This time-scale should provide both, short-term (daily) to mid-term (several years) transit time information (McDonnell et al., 2010). Due to the limited number of samples, all 98 samples were used for the optimization procedure, similar to Duvert et al. (2016). The TTD may be biased in that it does not capture very short (sub-daily) and long (decadal) transit time information due the sampling interval and due to the tracer suitability issue, respectively (McDonnell et al., 2010; Stewart et al., 2007; Stewart et al., 2010; Stewart et al., 2012).

We also used a time-invariant TTD modeling approach due to data limitations, since time-variant TTD modeling approaches typically require longer tracer records and/or higher sampling frequencies (Benettin et al., 2015; Benettin et al., 2013; Benettin et al., 2018; Birkel et al., 2015; Birkel et al., 2012; Duvert et al., 2016). Although headwater catchments—often characterized by high responsiveness and high seasonal variability in the climatic conditions—are known to be non-steady systems (McDonnell and Beven, 2014; Rinaldo et al., 2011), this approach is still feasible (Duvert et al., 2016; Seeger and Weiler, 2014), but time-variant approaches are becoming popular, e.g., Ala-aho et al. (2017b). The MTT estimate (8.2–10.5 years) must be carefully interpreted since $\delta^{18}O$ is increasingly recognized to be blind to the tail of the TTD and transit times longer than five years (Duvert et al., 2016; Kirchner, 2016a, b; Seeger and Weiler, 2014; Stewart et al., 2007; Stewart et al., 2010; Stewart et al., 2012).

The cumulated TRANSEP TTD at the threshold age of 56 days compared well to the $F_w$ estimated with the sine wave approach, which was already reported elsewhere (e.g., Stockinger et al., 2016). This may result from the facts that the GM underlied both approaches and that the same input was used, even though the shape parameter $\varphi$ differs (compare $\varphi$ values in Tab. 5-1 and Tab. 5-2), resulting in different TTDs. This led to the conclusion, that steady-state transit time models (like TRANSEP) likely provide unbiased mid-term transit time information (up to several months). Two main problems arose during the modeling procedure: i) runoff in 2014 has a markedly lower goodness of fit; ii) during the streamflow and tracer recession period in late 2015 the $\delta^{18}O$ of streamflow was not well emulated by TRANSEP. Up to now we are not able to explain these features.

Four degrees of uncertainty are worth being highlighted within the scope of our study:

- Structural uncertainty: We used a top-down modeling approach including a pre-defined model structure and tested it in our complex study catchment. The transfer functions were chosen by prior modeling experiments and the TPLR for runoff and the flexible GM for streamflow $\delta^{18}O$ were used. The latter allows for both, fast tracer throughputs and relatively long transit times (Kirchner et al., 2000), and did not assume a well-mixed reservoir, which was suitable for application in our catchment. Both transfer functions were proved best regarding the objective functions.
- Parameter uncertainty: Three out of five TRANSEP parameters were well-constrained during the Monte Carlo simulation ($\varphi$, $\tau_f$ and $\gamma$). $\tau_s$ and $\beta$ were less well-constrained, leading to the observed uncertainty of the TTD, RTD and storage estimates (see Fig. 5-5 and Tab. 5-2). The physical interpretation of the low $\alpha$ suggests a highly non-linear streamflow tracer response (Tab. 5-2, Hrachowitz et al., 2010).

- Input uncertainty: We used a single ESCIMO run as input data for TRANSEP and focused on the applicability of and the uncertainty within TRANSEP, but input uncertainty should be investigated in future studies as this represents an important source of uncertainty in TTD modeling, e.g., Duvert et al., (2016).

- Uncertainty due to the optimization procedure: The choice of the objective function was arbitrary, but after initial model experiments it became apparent that the splitting of the streamflow $\delta^{18}$O time series, as well as the higher weighted flow variability term (as used for the KGE), were relevant.

Future improvements can include i) the calibration of lumped parameter transit time models against $F_{yw}$ (e.g., Lutz et al., 2018), making the approach not independent, or ii) using a bottom-up modeling chain, starting with a perceptual model (and not a priori determined TTDs) or using time-variant TTDs.

### 5.5 Conclusion

We estimated the dynamic and mobile storage, the $F_{yw}$ (with the sine wave approach), and the TTD (with the convolution integral method using TRANSEP) in a highly glacierized catchment for the period 2014 to 2017. For input in the latter, we used lumped $\delta^{18}$O values of rain, snow and ice melt, as simulated with ESCIMO. Being the first study carried out in such a simulation setup and environment, we found large storages and a relatively high $F_{out}$, but contrarily also a high $F_{yw}$. This led to the conclusion that the basin behaves to some degree like a ‘Teflon basin’, especially because of the large contribution of fast transmitted ice melt, and to some degree like a huge sponge with a very much delayed release of water, especially due to the large potential subsurface water storage volume. The two behaviors are probably distributed more in space and less in time. We also found a highly non-linear streamflow tracer response. An appropriate input characterization is obligatory for both, the estimation of the $F_{yw}$ and the application of lumped parameter transit time models, i.e., accounting for the delayed contribution of snow and ice melt in glacierized catchments. Regarding mid-term transit time information (up to a few months), $F_{yw}$ estimated with TRANSEP and the sine wave approach were well comparable. Unfortunately, very short (sub-daily) and long (decadal) transit time information is not covered in the modeling approach, but we assumed that this might play an important role in the biogeochemical cycle of the catchment, especially if one considers very fast catchment responses to rain on ice events or the potential of deeper groundwater contribution to winter baseflow. Further studies to enhance the methodology for glacierized catchments may focus on time-variant TTDs and more detailed input characterization (e.g., higher sampling frequency and density, disaggregation/regionalization methods and accounting for isotopic fractionation of rain, snow and ice melt).
Acknowledgements

The Rofental is part of the LTSER platform Tyrolean Alps, which belongs to the national and international long term ecological research network (LTER-Austria, LTER Europe and ILTER). We gratefully thank Florian Hanzer for providing the meteorologic forcing data for ESCIMO. We thank the Hydrographic Service, the Zentralanstalt für Meteorologie and Geodynamik, and the Austrian Network of Isotopes in Precipitation and Surface Waters for their provision of hydrologic, meteorologic and isotopic data. We also acknowledge the numerous field assistants who helped collecting water samples in the Rofental over the years.
Supplement

Fig. 5-6: Monthly $\delta^2$H in precipitation (Obergurgl vs. Vent, 1972–1975).

Fig. 5-7: Overview scheme of modelling workflow. The grey boxes represent data used for model input, the blue boxes represent model output data and the white boxes are the models used in this study.
Tab. 5-3: ANIP station overview.

<table>
<thead>
<tr>
<th>Station</th>
<th>Longitude [°]</th>
<th>Latitude [°]</th>
<th>Elevation [m a.s.l.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Patscherkofel</td>
<td>11.45</td>
<td>47.2</td>
<td>2245</td>
</tr>
<tr>
<td>Oberburgl</td>
<td>11.02</td>
<td>46.87</td>
<td>1942</td>
</tr>
<tr>
<td>Gries_Brenner</td>
<td>11.52</td>
<td>47</td>
<td>1450</td>
</tr>
<tr>
<td>Laengenfeld</td>
<td>10.97</td>
<td>47.07</td>
<td>1180</td>
</tr>
<tr>
<td>Scharnitz</td>
<td>11.25</td>
<td>47.38</td>
<td>964</td>
</tr>
<tr>
<td>Schoppernau</td>
<td>10.2</td>
<td>47.3</td>
<td>835</td>
</tr>
<tr>
<td>Kufstein</td>
<td>12.15</td>
<td>47.57</td>
<td>491</td>
</tr>
<tr>
<td>Bregenz</td>
<td>9.73</td>
<td>47.48</td>
<td>430</td>
</tr>
</tbody>
</table>

Tab. 5-4: Monthly isotopic lapse rates.

<table>
<thead>
<tr>
<th>Month</th>
<th>δ¹⁸O slope [%°·1000 m⁻¹]</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan</td>
<td>-2.59</td>
<td>0.57</td>
</tr>
<tr>
<td>Feb</td>
<td>-2.35</td>
<td>0.46</td>
</tr>
<tr>
<td>Mar</td>
<td>-2.65</td>
<td>0.61</td>
</tr>
<tr>
<td>Apr</td>
<td>-1.98</td>
<td>0.79</td>
</tr>
<tr>
<td>May</td>
<td>-1.53</td>
<td>0.94</td>
</tr>
<tr>
<td>Jun</td>
<td>-1.58</td>
<td>0.94</td>
</tr>
<tr>
<td>Jul</td>
<td>-1.12</td>
<td>0.59</td>
</tr>
<tr>
<td>Aug</td>
<td>-1.14</td>
<td>0.62</td>
</tr>
<tr>
<td>Sep</td>
<td>-1.67</td>
<td>0.9</td>
</tr>
<tr>
<td>Oct</td>
<td>-2.05</td>
<td>0.93</td>
</tr>
<tr>
<td>Nov</td>
<td>-1.98</td>
<td>0.7</td>
</tr>
<tr>
<td>Dec</td>
<td>-2.37</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Tab. 5-5: Input data as used for TRANSEP.
Note: Table is too large to display (1461 rows), but can be download (https://www.mdpi.com/2306-5338/6/4/92).
Tab. 5-6: Fit statistics (a) and regression coefficients (b) of the sine wave approach for estimating the young water fraction.

(a) Fit statistics

<table>
<thead>
<tr>
<th></th>
<th>non-delayed monthly input</th>
<th>delayed daily input</th>
<th>delayed monthly input</th>
<th>streamflow</th>
</tr>
</thead>
<tbody>
<tr>
<td>R²</td>
<td>0.82</td>
<td>0.38</td>
<td>0.58</td>
<td>0.71</td>
</tr>
<tr>
<td>p value of F-statistic</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

(b) Regression coefficients

<table>
<thead>
<tr>
<th>Parameter</th>
<th>non-delayed monthly input</th>
<th>delayed daily input</th>
<th>delayed monthly input</th>
<th>streamflow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>value [%]</td>
<td>standard error [%]</td>
<td>p value [%]</td>
<td>value [%]</td>
</tr>
<tr>
<td>a</td>
<td>-4.37</td>
<td>0.33</td>
<td>&lt;0.001</td>
<td>-1.36</td>
</tr>
<tr>
<td></td>
<td>standard error [%]</td>
<td>0.22</td>
<td>&lt;0.001</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>p value [%]</td>
<td>0.77</td>
<td>0.43</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>value [%]</td>
<td>standard error [%]</td>
<td>p value [%]</td>
<td>value [%]</td>
</tr>
<tr>
<td>b</td>
<td>-3.22</td>
<td>0.34</td>
<td>&lt;0.001</td>
<td>-2.78</td>
</tr>
<tr>
<td></td>
<td>standard error [%]</td>
<td>0.11</td>
<td>&lt;0.001</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>p value [%]</td>
<td>&lt;0.001</td>
<td>-2.68</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>value [%]</td>
<td>standard error [%]</td>
<td>p value [%]</td>
<td>value [%]</td>
</tr>
<tr>
<td>k</td>
<td>-15.22</td>
<td>0.24</td>
<td>&lt;0.001</td>
<td>-16.17</td>
</tr>
<tr>
<td></td>
<td>standard error [%]</td>
<td>0.19</td>
<td>&lt;0.001</td>
<td>-15.9</td>
</tr>
<tr>
<td></td>
<td>p value [%]</td>
<td>-0.001</td>
<td>-14.53</td>
<td>0.19</td>
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<tr>
<td></td>
<td>value [%]</td>
<td>standard error [%]</td>
<td>p value [%]</td>
<td>value [%]</td>
</tr>
</tbody>
</table>
6 A perceptual model of catchment functioning

6.1 Overview of the data basis

The individual studies in this thesis (Chapter 3-5) and ongoing research led to a refined perception of glacierized high-elevation catchment functioning (i.e. the partitioning, storage and release of water). This work helps to better understand the transit time of water through the catchment and to improve the knowledge of timing and amount of input source components such as rain, snowmelt and ice melt of streamflow. All these advances in understanding enabled to develop a perceptual model of the Rofenache catchment that qualitatively describes the key hydrological processes. Perceptual models are based on the analyzed data sets and on field interpretation, as well as on the researcher’s expertise (Beven, 2012; Dunn et al., 2008; Refsgaard and Henriksen, 2004). Its suitability and transferability remains to be tested with additional data and in other glacierized catchments.

The average tracer and runoff response of the Rofenache, as indicated by measured discharge (Q), EC and δ18O for the period 2014 to 2018 can be seen in Fig. 6-1. The variability in EC (range: 200 µS/cm), δ18O (range: 4 ‰) and daily Q (range: 35 m³/s) (Fig. 6-1a and c) is common in similar catchments (Engel et al., 2016; Penna et al., 2017; Zuecco et al., 2019). The marked sub-daily variability of the three variables throughout the ablation period is not visible from Fig. 6-1 (Chapter 3 and 4). The marked scattering of the points in Fig. 6-1a results from day-to-day (short-term), seasonal (intermediate-term) and year-to-year (long-term) variability (Chapter 5). Short-term variability of the above-mentioned variables can be attributed to the very fast on- and off-switch of dominant processes (e.g. new snow on bare glacier ice immediately stops ice melt production and leads to increase in EC and decrease in Q). Intermediate-term variability is controlled by seasonally changing environmental conditions (e.g. a snow-rich winter followed by warm spring leads to a distinct trough in δ18O). Long-term variability is affected by climatic variability (e.g. consecutive warm years tend to shift the δ18O curve up). The correlation of EC and δ18O is typical for melt-dominated catchments (Engel et al., 2016; Penna et al., 2017; Zuecco et al., 2019) and can be seen in Fig. 6-1b. Distinct periods with strong negative and positive correlation, but also periods without correlation become obvious.
6.2 Generalizing the tracer and runoff response and related processes

The findings of this thesis contribute to the perception of how the catchment functions by focusing on runoff generation, water flow pathways, as well as the tracer and runoff response of the stream. Three important features of the perceptual model relate to and highlight significant key hydrological processes of glacierized basins (Fig. 6-2a): 1) the trough in the streamflow δ¹⁸O curve marks the period of the highest snowmelt fraction in streamflow during the peak snowmelt period; 2) the increase in streamflow δ¹⁸O concomitant with further decrease in streamflow EC (i.e. a switch from positive to negative correlation) can be attributed to the transition from the snowmelt to the ice melt-dominated streamflow response; 3) the trough in the streamflow EC curve depicts the highest ice melt fraction in streamflow (peak glacier melt period).
Six characteristic stages (or periods) of the hydrological year are described for a high-elevation catchment with a glacial flow regime:

- The winter baseflow period (Fig. 6-2b) is characterized by the recession of Q and streamflow $\delta^{18}$O, as well as by the rise in streamflow EC. All three variables approach an almost steady value towards the end of the period and reveal a very low variability. The catchment is completely snow-covered and after the freeze-up period in a frozen state (no inputs from rain, snowmelt or ice melt). The outflow from the subsurface reservoir (mainly groundwater flow from talus, moraines, rock glaciers and fractured bedrock aquifers) generates streamflow and controls the flow (very low Q) as well as its tracer signature (high EC and intermediate $\delta^{18}$O values).

- During the early snowmelt period (Fig. 6-2c), streamflow is additionally composed of new snowmelt (low melt rates) with low EC and low $\delta^{18}$O values generated from the seasonal snowpack in the lower area of the catchment. This leads to a positively correlating decrease in streamflow EC and streamflow $\delta^{18}$O and to a slight increase in Q. The variability of the three streamflow variables is also increasing. Infiltration due to snowpack outflow, as well as onset of overland and activation of subsurface flow paths (interflow)--all three depending on the system state of the soil (frozen, wetness)--are typical processes associated with this period.

- The peak snowmelt period (Fig. 6-2d) consists of further depletion of the snow-covered area and high snowmelt rates, leading to the maximum snowmelt fraction in streamflow. Interflow and groundwater flow, as well as overland flow are enhanced and play dominant roles in the streamflow generation processes. EC and $\delta^{18}$O of
streamflow are further decreasing (large input of snowmelt with low EC and low δ^{18}O values) with the annual trough in δ^{18}O and intermediate variability for both variables. Q reveals intermediate values with a intermediate variability.

- The lower area of the glaciers become snow-free during the transition from the snowmelt- to the ice melt-dominated period (Fig. 6-2e) which leads to intensified meltwater input into the system (additional ice melt with very low EC and intermediate δ^{18}O values). Streamflow EC decreases further and streamflow δ^{18}O starts to increase, shifting their correlation coefficient. Open-channel flow is enhanced.

- The annual trough in streamflow EC, strongly increasing streamflow δ^{18}O values, annual peak flow and high variability in streamflow EC and Q characterize the peak glacier melt period (Fig. 6-2f). The seasonal snow-cover ceases and streamflow compiles of the largest ice melt fraction during the hydrological year. The glaciers build up an efficient drainage system and favor fast flow velocities by supra-, en- and subglacial channels, pipes and sheet flow, leading to enhanced open-channel flow in streams. Hence quick runoff and tracer response dominate streamflow.

- The last period (Fig. 6-2g) is based on ice melt supply with interchanging aperiodic interruption of rainfall-dominated periods or snowfall. Melt production is energy-limited and Q decreases steadily (recession flow) or drops fast due to the new snow cover starting to build up. Streamflow EC rises and streamflow δ^{18}O reveals the annual peak due to high δ^{18}O values of contributing rain. Runoff generation can be complex during this period due to all three input sources occurring in the same period (ice melt, rain, snowmelt), with alternating dominance of channel flow (ice melt and/or rain), interflow (snowmelt or light rain) or overland flow (heavy rain).

Overall, the tracer-hydrologic behavior of streamflow is dominantly characterized by distinct diurnal and seasonal fluctuations of the response variables Q, EC and δ^{18}O. This characteristic is driven by the periodic energy-availability for melt. Aperiodic variations can superimpose or supersede the cyclic characteristic, also during the peak snowmelt to the peak glacier melt period (Fig. 6-2d-f). These are controlled by heavy rainfall events, for example, as occurred on 24 August 1987 which produced the Q_{max} (102 m^3/s) at the gauging station ‘Vent’ during the period 1967-2018. Long term variations at interannual or longer time scales are driven by climatic variation or change and can, but must not be periodically. Aperiodic variations (e.g. tracer and runoff response to heavy rainfall) or climatic change (trends) are underrepresented or not depicted in the perceptual model, respectively.

### 6.3 Discussing the suitability of the perceptual model

Perceptual models in hydrology typically represent a coarse level of detail, neglect point or small-scale processes, but accentuate the perceived dominant and important processes at the larger scale to understand how the catchment system works (Wagener et al., 2007). The perceptual model described in Chapter 6.2 can therefore be seen as the simplified average behavior of the catchment. It is obvious that the timing of the three described streamflow features (δ^{18}O trough, correlation shift of EC-δ^{18}O, EC trough), as well as the harsh
A perceptual model of catchment functioning

delimitation of the periods can shift from year to year and do not apply for every single year since their timing depends on the individual environmental conditions (Ambach et al., 1976). Among the many perceptual models in hydrology that can be found in the literature (e.g. Anderson and Burt, 1990; Beven, 2012), only the least of them were derived by means of environmental tracers for glacierized high-elevation catchments. An older variant (no graphic) for the Rofental was described by Ambach et al. (1976) with a strong focus on the ablation period; it served as a starting point to build up the proposed model. The periods were more roughly classified in Ambach et al. (1976) based on the streamflow $\delta^2$H deviation from mean streamflow $\delta^2$H during the winter accumulation period ($\delta^2$H$_{wi}$): beginning of ablation (snowmelt; $\delta^2$H $< \delta^2$H$_{wi}$), summer ablation (ice melt; $\delta^2$H $> \delta^2$H$_{wi}$), winter accumulation ($\delta^2$H$_{wi}$). In the new variant proposed in this thesis, more periods were classified (n=6) by the dual tracer behavior of EC and $\delta^{18}$O, different temporal scales of variability were described (sub-daily to year-to-year), the non-ablation period received intensified awareness, and non-melt-related processes (rainfall events), as well as other runoff generation processes that occur on the non-glacierized area and beneath the surface were included (overland flow, interflow, groundwater flow). The outlined perceptual model of the Rofental also shows some similarities with that one described by Penna et al. (2017) for an adjacent catchment (Saldur River catchment, Italy) with a lower fraction of glacierized area. In contrast to the Rofental (glacial flow regime due to 35 % glacierized area), their test catchment’s trough in EC due to ice melt contribution is less pronounced, since the flow regime is nivo-glacial (12 % glacierized area). Richards and Moore (2003) also describe a further drop of EC related to the decreasing snowmelt fraction and increasing ice melt fraction of streamflow in their 26 % glacierized catchment (Place Creek catchment, Canada) during the ablation period. Penna et al. (2017) describe a strong positive correlation for monthly grouped EC-\(\delta^2\)H pairs during the snowmelt period and a weak negative correlation during the glacier melt period. This also supports the hypothesis that the shift from positive to negative correlation of both variables during the ablation periods marks the increasing dominance of the ice melt component in streamflow (i.e. a proxy for the timing when glaciers start to become snow-free).

Future work includes the refinement of the perceptual model by i) extending the time series, ii) adding geochemical tracers, iii) adding deuterium excess (or line-conditioned excess), incorporating iv) input water sources (ice melt, snowmelt, rain), as well as v) water ages. This new proposed hypothesis of catchment functioning should then be tested with new data, but the described processes should also be incorporated in numerical modelling studies. Further, its representativeness should be tested in other glacierized high-mountain catchments. Considering climate change, further recession of glaciers and decreasing relative contribution of ice melt to streamflow can be expected (IPCC, 2019). Extending the time series in the Rofental, as well as investigating other catchments can hence also help to enhance the understanding of future runoff generation and composition. Questions like ‘How does a shift from the ice melt- to the snowmelt-dominated flow regime propagate to the tracer response, alter the key hydrologic processes and what can we learn from it?’ may shed light on the future headwater supply important for many downstream water users.
7 Synthesis

7.1 Conclusion

The overarching aim of this thesis was to better understand the hydrologic functioning of glacierized high-elevation catchments under consideration of varying system states during different periods of the hydrologic year. Therefore the following objectives were investigated:

- the snow and ice melt spatio-temporal tracer variability at various scales,
- the quantification of discharge components, and
- the streamflow transit time and catchment subsurface storage.

Combining tracer-based monitoring and modelling methods helped to gain a deeper process-based understanding of the Rofental catchment functioning as a representative for glacierized high-elevation catchments.

Debates on the snow ablation period

The event-based investigation during a snow ablation period at different system states, i.e. an early melt and a peak melt event (Chapter 3), gained insight into the spatio-temporal dynamic of the snowmelt isotopic composition in relation to the melt rate. Sampling time and location is very important for the interpretation of water samples (see also Penna et al., 2018), and using the observed data as input in mixing models revealed significant differences in the results. Analysing events at this resolution (e.g. sampling sub-daily snowmelt) in such remote environments is at the front end of science, since mostly seasonal estimates (e.g. using single snow cores as input characterization) were used in the literature which might miss the short-term dynamics prescribed to fractionation processes. The high-resolution analysis is recommended if one aims at the right reasons (Kirchner, 2006) instead of only separating streamflow into its components. A two-component mixing model (pre-event water: slow subsurface contribution of old water stored in the catchment before the onset of snowmelt characterized by the winter baseflow tracer signature; event water: fraction of new snowmelt water input into the system during the event) was applied and the inferred pattern of system behavior is the spill of old water at the beginning of the snowmelt period concomitant with gradual fill up of the subsurface reservoir by new snowmelt which resulted in very high snowmelt fractions during the peak snowmelt period (up to 78 %; Fig. 3-4). Overland flow was observed in the catchment, but the contribution was relatively low, resulting in restricted importance of this flow path. Furthermore, the coupling with an energy-based surface snowmelt model which provided areal snowmelt rates helped to provide robust snowmelt rates to weight the snowmelt isotope composition obtained at the plot scale. The advantage of combining numerical model results with empirical-based isotope measurements also helped to perform a spatial hydrograph separation (e.g. the snowmelt component of streamflow which was produced on the south-facing slope of the catchment). Capturing the total variability in an almost 100 km$^2$ area is rather unrealistic, therefore the combined methodology and the detailed uncertainty analysis helped in interpreting the results.
Debates on the glacier ablation period

A data-driven modelling approach was used to separate the streamflow in a nested subcatchment of the Rofental (17.1 km$^2$) during a glacier ablation period at the event scale (Chapter 4). Therefore a three-component mixing model (new ice melt, antecedent rain, and old groundwater) was applied with EC and $\delta^{18}$O during six events (each a day long) characterized by different antecedent precipitation and ice melt rates. This shed light into new insights of streamflow components since numerical modelling studies, as often applied in such environments, typically address only celerity (Frenierre and Mark, 2014; McDonnell and Beven, 2014) and produce often very high ice melt fractions of streamflow. These miss the groundwater recharge due to ice melt, which can be significant, too (e.g. Dochartaigh et al., 2019) and hence do not account for flow path in, beneath and in front of a glacier. On the other side, tracer-based mixing models integrally do account for these flow paths, provided that one samples the appropriate end-members. Therefore the estimated ice melt fractions of streamflow were quite surprising in 2016 (up to 76 %; Fig. 4-9), but more important, groundwater was the dominant contributor during these events (49 % on average). The high spatio-temporal frequency of the measurements led to a relatively comprehensive data set (in total 51 ice melt samples could be compiled for six days), which could be used to analyse the sensitivity in applying the mixing model. The sensitivity was not as marked as for snowmelt, but revealed an effect related to the temporal variation throughout the season, especially for events with large ice melt fraction of streamflow. Sub-daily and spatial variation at the small scale had negligible influence on estimated ice melt fractions. The results not only reveal the importance of groundwater, but also that of rainfall-runoff dynamics, which both might play an even more important role in the future under the light of climate change. Some of the stream samples in the dual tracer space, the mixing diagram (Fig. 4-7), tend towards the rain end-member (antecedent rain a few days before the sampling represented by bulk samples) which resulted in an average rain fraction of 16 % for the six events. This means, the catchment contributes rain—which was stored for a few days—to streamflow, even during rain-free ice melt days. The shallow groundwater end-member is characterized by the mean winter baseflow tracer signature and represents the old water stored in the subsurface. Rain and ice melt end-members represent the intermediate (a few days) and the event time scale, respectively.

Evidence for the transformative role of high-elevation catchment transit time and storage

Chapter 5 is directly related to the question ‘Why do streams respond so quickly to precipitation inputs when stormflow is so old, and what is the transit time distribution of water in the terrestrial water cycle?’ as one of the ‘23 unsolved problems in hydrology’ postulated by Blöschl et al. (2019). An energy-balance surface model combined with a lumped tracer-aided transit time model was used for estimating water age components of streamflow and subsurface storage volume. This analysis unifies the tracer-based monitoring and modelling methods implemented in a design at the catchment scale for a period of four successive years. Because time-invariant transit time model approaches are often contested, the young water fraction (Kirchner, 2016a, b) was additionally calculated. The energy-balance
approach was enhanced, so that isotope ratios could be used as input for the transit time model, but also as input for the calculation of the young water fraction. Both age component approaches yielded similar results in the fraction of streamflow up to 3 months old, i.e. 42-47% of water during the period 2014 to 2017. The mean transit time, although with the potential to be biased (Stewart et al., 2010; Stewart et al., 2012), was estimated at 9.5 years, resulting in a storage volume of almost 14 m (water equivalent). This led to the conclusion that the catchment can be pictured by both, a Teflon pan (e.g. due to large volumes of fast transmitted ice melt) and a huge sponge (e.g. large volumes can be stored in talus, rock glaciers, alluvium, moraines and fractured bedrock). By using this outlined methodology, such estimates could initially be published for a glacierized high-elevation catchment, contributing to the transformative aspect of groundwater contribution in (high-)mountain catchments (Hayashi, 2019).

7.2 Open questions

Spatio-temporal resolution of input tracer signatures

Although there is a decreasing tendency of measurement campaigns in hydrology, also named ‘the dying art’ by Burt and McDonnell (2015), tracer hydrologist keep on to sample water in headwater catchments (Penna et al., 2018), not only for the purpose of modelling studies, but also because we still do not understand the hydrological processes of streamflow generation mechanisms in high-mountain catchments sufficiently. The collected data helps to formulate new hypotheses of glacierized high-elevation catchment functioning (Pfister and Kirchner, 2017). Since tracer sampling and analyses require much effort (or sometime are not possible) and are cost expensive, disaggregation or modelling techniques should be applied and enhanced. The input tracer characterization is not straightforward in glacierized catchments, because snowmelt and ice melt are additional input sources (not only rain) which must be accounted for. The temporal isotopic evolution from snow to ice and meltwater, as well as the spatial redistribution are not well understood and hard to sample, but essential as input for both, tracer-based and tracer-aided models.

Regarding the spatial variability, e.g. the elevation-dependency, the snow or ice melt isotopic lapse rate could be analysed as a starting point. According to the glacier flow and isotope ratio distribution model of Lawson and Kulla (1978) sampling at equilibrium line altitude could reveal the mean ice melt isotope ratio. This hypothesis is still to be tested and, if verified, would make the lapse rate measurements redundant and could serve as a data-reduced variant for the sampling design.

Process-based numerical modelling, on the other side, requires to understand the spatio-temporal pattern and the isotopic evolution due to fractionation at the small scale. Pioneering work is published by Ala-aho et al. (2017a) in which they simulated the isotopic evolution of snow including fractionation effects and tested it at three small headwater catchments at the grid scale (Ala-aho et al., 2017b). Such an application is still not available for ice-melt dominated regions or high-elevation catchments with deep snow packs. This is likely due to the fact that ice melt isotope ratios are more complex to model (more freeze-thaw cycles),
hence the sampling-intensive derivation of the isotopic lapse rate of ice melt was used (e.g. He et al., 2019).

Streamflow ages

Dynamic (or time-variant) transit time distribution estimations of streamflow are not described in the literature for glacierized high-elevation catchments, as done for many humid temperate catchments (e.g. Hrachowitz et al., 2016). This is important, since the flow pathways during different periods (rain vs. snowmelt vs. ice melt) and hence the transit times likely differ also for glacierized catchments. A first approach could include the investigation by a time-invariant transit time distribution for different events (or time slices) during the hydrologic year and compare the resulting transit time distributions, as done for the snowmelt period by Lyon et al. (2010) for 15 northern boreal catchments.

The new water fraction or transit time distribution can also be estimated with the ensemble hydrograph separation approach, as postulated recently by Kirchner (2019). The fraction of streamflow (e.g. same-day input) during different periods of the hydrologic year would provide another tool to investigate the above-mentioned characteristics without the need to prescribe the transfer function (shape of the TTD). Either way, a prerequisite is the characterization of input isotopic signatures as described in the section ‘Spatio-temporal resolution of input tracer signatures’.

Input source components of streamflow

A neglected research field in catchment hydrology of glacierized high-mountain regions is related to rainfall: Which flow paths does rain take to the stream? How much rain do we see in the stream? What is the transit time distribution of rain? There are only a few studies which address this underrepresented topic (e.g. Vaughn & Fountain, 2005; Dahlke et al., 2014). Applying geochemical tracer could be an important methodology to further investigate this topic.

Investigating longer temporal extents (i.e. seasonal, multiple years) is also important for estimating the tracer-based input water sources with a mixing model as done regularly with conceptual models (Frenierre and Mark, 2014). This would also support a comparison by providing an alternative strategy and independent method. The potential of using two isotope tracers, which are mostly unaltered by subsurface storage, e.g. $\delta^{18}$O and deuterium excess, (or line-conditioned excess) could hold potential as already exploited by Boral et al. (2019) or Li et al. (2019). This would enable the use of a classical mixing model with three components (ice, rain, snow) since these components often span a triangle in the dual tracer space.

A very important question is where the high-mountain stream water during winter low-flow conditions comes from. This is even more important as the alpine aquifers have potential to compensate for the declining ice melt contribution (Castellazzi et al., 2019). Again, the classical three-component mixing model as described above could be applied to investigate this question.
Flow paths of water

The role of the high-mountain aquifers (or hydrogeological response units) has to be further employed, as postulated by Hayashi (2019). This includes studying surficial aquifers (talus, moraines, and rock glaciers) as well as storage in bedrock depressions or in fractured bedrock. The role of deep bedrock aquifers is almost unknown (Vincent et al., 2019). High-mountain groundwater can be stored temporarily in these aquifers and these can have potential to compensate the decreasing ice melt contribution, as some studies already picked up (Castellazzi et al., 2019; Evans et al., 2015; Jones et al., 2019; Ó Dochartaigh et al., 2019; Saberi et al., 2019; Somers et al., 2019). Tracer studies may help to identify the transit times and flow paths during groundwater-fed streamflow periods (i.e. winter baseflow) and could help to overcome the restriction of limited subsurface data. Unless there are no future drilling campaigns, sampling springs and winter baseflow holds the only potential to gain a deeper understanding of the hydrogeology.
References


Gruber, S.: A mass-conserving fast algorithm to parameterize gravitational transport and deposition using digital elevation models, Water Resources Research, 43, n/a-n/a, 2007.


Helfricht, K.: Analysis of the spatial and temporal variation of seasonal snow accumulation in Alpine catchments using airborne laser scanning. Basic research for the adaptation of spatially distributed hydrological models to mountain regions, PhD, University of Innsbruck, Innsbruck, 134 pp., 2014.


IPCC: Summary for Policymakers, Cambridge, United Kingdom and New York, NY, USA, 2013.


Keller, R.: The international hydrological decade — The international hydrological programme, Geoforum, 7, 139-143, 1976.


Kirchner, J. W.: Getting the right answers for the right reasons: Linking measurements, analyses, and models to advance the science of hydrology, Water Resources Research, 42, 2006.


Laudon, H., Seibert, J., Köhler, S., and Bishop, K.: Hydrological flow paths during snowmelt: Congruence between hydrometric measurements and oxygen 18 in meltwater, soil water, and runoff, Water Resources Research, 40, n/a-n/a, 2004.


Lundquist, J. D., Dettinger, M. D., and Cayan, D. R.: Snow-fed streamflow timing at different basin scales: Case study of the Tuolumne River above Hetch Hetchy, Yosemite, California, Water Resources Research, 41, n/a-n/a, 2005.


Marke, T. and Strasser, U.: Continuous meteorological observations at station Latschbloder in 2016. In: In supplement to: Strasser, Ulrich; Braun, Ludwig N; Escher-Vetter, Heidi; Juen, Irmgard; Kuhn, Michael; Marke, Thomas; Maussion, Fabien; Mayer, Christoph; Nicholson, Lindsey; Niederscheider, Klaus; Sailer, Rudolf; Stötter, Johann; Weber, Markus; Kaser, Georg (submitted): The Rofental: a high Alpine research basin (1890 m - 3770 m a.s.l.) in the Ortal Alps (Austria) with over 150 years of hydro-meteorological and glaciological observations. Special Issue: Hydrometeorological data from mountain and alpine research catchments; 04 Aug 2015-30 Sep 2017; Guest editors: J. Pomeroy and D. Marks, Earth System Science Data Discussions, 27 pp, PANGAEA, 2017.


Schuler, T.: Investigation of water drainage through an alpine glacier by tracer experiments and numerical modeling, Ph.D., Swiss Federal Institute of Technology in Zurich, Switzerland, 140 pp., 2002.


References


