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Controls on spatial and temporal variability of streamflow and hydrochemistry in a glacierized catchment

Running title: Controls on streamflow and hydrochemistry in a glacierized catchment

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Abstract

The understanding of the hydrological and hydrochemical functioning of glacierized catchment requires the knowledge of the different controlling factors and their mutual interplay. For this purpose, the present study was carried out in two sub-catchments of the Sulden River catchment (130 km², Eastern Italian Alps) in 2014 and 2015, characterized by similar size but contrasting geological setting. Samples were taken at different space and time scales for analysis of stable isotopes of water, electrical conductivity, major, minor and trace elements.

At the monthly sampling scale for different spatial scales (0.05 – 130 km²), complex spatial and temporal dynamics such as contrasting EC gradients in both sub-catchments were found. At the daily scale, for the entire Sulden catchment the relationship between discharge and electrical conductivity showed a monthly hysteretic pattern. Hydrometric and geochemical dynamics were controlled by an interplay of meteorological conditions and geological heterogeneity. After conducting a PCA analysis, the largest share of variance (36.3 %) was

explained by heavy metal concentrations (such as Al, V, Cr, Ni, Zn, Cd, Pb) during the melting period while the remaining variance (16.3 %) resulted from the bedrock type in the upper Sulden sub-catchment (inferred from EC, Ca, K, As and Sr concentrations). Thus, high concentrations of As and Sr in rock glacier outflow may more likely result from bedrock weathering. Furthermore, nivo-meteorological indicators such as maximum daily global solar radiation, three day maximum air temperature, and 15 day snow depth differences could explain the monthly conductivity and isotopic dynamics best. The decrease of snow depth calculated for different time lengths prior to the sampling day showed best agreements with conductivity and isotopic dynamics when time lengths varied. These insights may help to better predict hydrochemical catchment responses linked to meteorological and geological controls and to guide future classifications of glacierized catchments according to their hydrochemical characteristics.

1 Introduction

Runoff from glacierized catchments is an important fresh water resource to downstream areas (Kaser et al., 2010; Viviroli et al., 2011). High-elevation environments face rapid and extensive changes through retreating glaciers, reduced snow cover, and permafrost thawing (Harris et al., 2001; Dye, 2002; Beniston, 2003; Galos et al., 2015). This will have impacts on runoff seasonality, water quantity and water quality (Beniston 2006; Ragettli et al., 2016; Gruber et al., 2017). It is therefore of uttermost importance to better understand the behaviour of high-elevation catchments and their hydrological and hydrochemical responses at different spatial and temporal scales in view of water management, water quality, hydropower, and ecosystem services under the current phase of climate change (Beniston, 2003; Viviroli et al., 2011; Beniston and Stoffel, 2014).

In general, the hydrological response of catchments (i.e. runoff dynamics) are controlled by heterogeneous catchment properties (Kirchner, 2009), which become more diverse in catchments with large complexity of various landscape features, as it is the case of mountainous, high-elevation glacierized catchments (Cook and Swift, 2012). In fact, those catchments are deemed as highly dynamic geomorphological, hydrological and biogeochemical environments (Rutter et al., 2011). Understanding the interactions of controls driving the catchment response represents the key focus of studies in catchment hydrology

(Troch et al., 2015). The advances of tracer and isotope hydrology made during the last decades can substantially contribute to this objective, in order to gain more insights into the variability of different runoff components (Vaughn and Fountain, 2005; Maurya et al., 2011; Xing et al., 2015), catchment conceptualization (Baraer et al., 2015; Penna et al., 2017), and sensitivity to climate change (Kong and Pang, 2012).

In general, the main controls of hydrological and hydrochemical catchment responses are represented by climate, bedrock geology, surficial geology, soil, vegetation, and topography with drainage network (Devito et al., 2005; Carrillo et al., 2011; Williams et al 2015) and catchment shape (Sivapalan 2003). First, a major role is attributed to the global and regional climate, having strong impacts on mountain glaciers and permafrost, streamflow, water quality, water temperature, and suspended sediment yield (Milner et al., 2009; Moore et al., 2009; IPCC, 2013). The impact of climate is difficult to assess because it requires long time windows (e.g., decades), whereas meteorological drivers interact at a smaller temporal scales and thus are easier to address. Among different meteorological drivers, radiation fluxes at the daily time scale were identified as main energy source driving melting processes in glacierized catchments in different climates (Sicart et al., 2008). Beside radiation, air temperature variations correlate well with runoff under the presence of snow cover (Swift et al., 2005) and may affect streamflow seasonality when specific thresholds are exceeded (Cortés et al., 2011).

With respect to geology, it sets the initial conditions for catchment properties and drives its evolution (Carrillo et al., 2011). The geological setting strongly controls catchment connectivity, drainage, and groundwater discharge (Farvolden 1963), runoff response (Onda et al., 2001), residence time (Katsuyama et al., 2010), hydrochemistry during baseflow conditions (Soulsby et al., 2006a) and melting periods (Hindshaw et al., 2011), and subglacial weathering (Brown and Fuge, 1998). Also geomorphological features such as talus fields may affect streamflow and water quality, resulting from different flow sources and flow pathways (Liu et al., 2004). Catchment storage, as determined by both geology and topography, was found to impact the stream hydrochemistry as well (Rinaldo et al., 2015).

The hydrological conditions of the catchment are also a relevant driver of hydrological response and commonly refer to the antecedent soil moisture conditions to describe the state of the catchment and represent the hydrological connectivity (Uhlenbrook and Hoeg, 2003; Freyberg et al., 2017). Specifically in high elevation and high latitude catchments, also permafrost thawing affects the hydrological connectivity (Rogger et al., 2017), leading to a strong control on catchment functioning as it drives the partitioning, storage and release of water (Tetzlaff et al., 2014). In more detail, retreating permafrost may also result in distinct geochemical signatures (Clark et al., 2001) and the release of heavy metals being previously stored in the ice (Thies et al., 2007; Krainer et al., 2015). This does not affect only the water quality but also the aquatic biota such as macroinvertebrate communities in these environments (Milner et al., 2009). Different weathering processes between the subglacial and periglacial environment can be found, resulting in a shift in chemical species and concentrations in the water (Anderson et al., 1997).

However, only few studies have investigated the geological, meteorological, and topographic controls on catchment response and stream water hydrochemistry in glacierized or permafrost-dominated catchments (Wolfe and English, 1995; Hodgkins, 2001; Lewis et al., 2012).

In this paper, we aim to fill this gap presenting data from a two year monitoring campaign where samples for stable isotopes of water, electrical conductivity (EC), major, minor and trace elements analysis were collected for two nearby glacierized catchments in the Eastern Italian Alps, characterized by similar size and climate and but contrasting geological setting.

The present study builds up on the following hypotheses: (1) bedrock-specific geochemical signatures reveal the geographic origin of water sources, (2) dilution effects and isotopic depletion in stream hydrochemistry are explained better by nivo-meteorological indicators controlling melt processes by radiation and air temperature than by precipitation-related indicators and (3) catchment controls not varying in short periods (such as geology and topography) lead to spatial variation in hydrochemistry while short-term controls (such as meteorological conditions) affect the temporal variations of hydrochemistry.

Specifically, we aim to:

- assess the spatio-temporal variability of the hydrochemical signature of stream water during melting and baseflow conditions;
- identify the hydrochemical signature of thawing permafrost and its role on stream water;

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- analyse the capability of nivo-meteorological indicators to describe the hydrochemical signature of stream water.

2 Study area and instrumentation

2.1 The Sulden river catchment

The study was carried out in the Sulden/Solda River catchment, located in the upper Vinschgau/Venosta Valley (Eastern Italian Alps) (Fig. 1). The size of the study area is about 130 km² defined by the stream gauge station of the Sulden River at Stilfserbrücke/ Ponte Stelvio (1110 m a.s.l.). The highest elevation is represented by the Ortler/ Ortlers peak (3905 a.s.l.) within the Ortles-Cevedale group. A major tributary is the Trafoi River, joining the Sulden River close to the village Trafoi-Gomagoi. At this location, two sub-catchments, namely Sulden and Trafoi sub-catchment (75 and 51 km², respectively) meet.

The study area has a current glacier extent of about 17.7 km² (14 % of the study area) and is slightly higher in the Trafoi than in the Sulden sub-catchment (17 % and 12 %, respectively). Main glacier tongues in the study area are represented by the Madatsch glacier (Trafoi sub-catchment) and Sulden glacier (Sulden sub-catchment). Geologically, the study area belongs to the Ortler-Campo-Cristalin (Mair et al., 2007). While permotriassic sedimentary rocks dominate the Trafoi sub-catchment, Quarzphyllite, Orthogneis, and Amphibolit are present in the Sulden sub-catchment. However, both catchments share the presence of orthogneis, paragneis and mica schist from the lower reaches to the outlet. Permafrost is sparsely located between 2400 and 2600 m a.s.l. and more frequent above 2600 m a.s.l. (Boeckli et al., 2012). Climatically, the mean annual air temperature is about -1.6 °C and the mean annual precipitation is about 1008 mm (2009 - 2016) at 2825 m a.s.l. (Hydrographic Office, Autonomous Province of Bozen-Bolzano). Due to the location of the study area in the inner dry Alpine zone, these precipitation amounts are relatively low compared to the amounts at similar elevation in the Alps (Schwarb, 2000). Further climatic data regarding the sampling period of this study are shown in Table 1.The study area lies within the National Park “Stelvio / Stilfser Joch” but it also includes ski slopes and infrastructures, as well as hydropower weirs.

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2.2 Meteorological, hydrometric and topographical data

Precipitation, air temperature, humidity and snow depth is measured by an ultrasonic sensor at 10 min measuring interval at the automatic weather station (AWS) Madritsch/Madriccio at 2825 m a.s.l. (run by the Hydrographic Office, Autonomous Province of Bozen-Bolzano). We take data from this station as representative for the glacier in the catchment at similar elevation. At the outlet at Stilfserbrücke/Ponte Stelvio, water stages are continuously measured by an ultrasonic sensor (Hach Lange GmbH, Germany) at 10 min measuring interval and converted to discharge via salt dilution/photometric measurements (measurement range: 1.2 – 23.2 $m^3 s^{-1}$; n=22). Turbidity is measured by a SC200 turbidity sensor (Hach Lange GmbH, Germany) at 5 min measuring interval. EC is measured by a TetraCon 700 IQ (WTW GmbH, Germany) at 1 second measuring interval. Both datasets were resampled to 10 min time steps. All data used in this study are recorded and presented in solar time.

Topographical data (such as catchment area and 50 m elevation bands) were derived from a 2.5 m DEM using GIS processing (ArcGIS 10, ESRI).

2.3 Tracer sampling and analysis

Continuous stream water sampling at the outlet was performed by an automatic sampling approach using an ISCO 6712 system (Teledyne Technologies, USA). Generally, daily water sampling took place from mid-May to mid-October 2014 and 2015 (on 331 days) at 23:00 to ensure consistent water sampling close to the discharge peak and respecting its seasonal variation. In addition, grab samples from different stream locations, tributaries, and springs in the Sulden and Trafoi sub-catchments and the outlet were taken monthly from February 2014 to November 2015 (Table 2). Samples were collected approximately at the same time (within less of an hour of difference) on all occasions. In winter, however, a different sampling time had to be chosen for logistical constraints (up to four hours of difference between both sampling times).However, this did not produce a bias on the results due to the very limited variability of the hydrochemical signature of water sources during winter baseflow conditions. Two active rock glaciers, located on Quarzphyllite bedrock in the upper Sulden sub-catchment, were selected to represent meltwater from permafrost. At the base of the steep rock glacier front, three springs at about 2600 m a.s.l. were sampled monthly from July to September 2014 and July to October 2015. Snowmelt water was collected as dripping water from snow patches from April to September 2014 and March to October 2015 (n = 48 samples), mainly located on the west to north-facing slopes of the Sulden sub-catchment and at the head of the valley in the Trafoi sub-catchment. Glacier melt water was taken only at the eastern tongue of the Sulden glacier from July to October 2014 and 2015 (n = 11 samples) for its safe accessibility. Precipitation samples were derived from bulk precipitation collectors, built according to the standards of the International Atomic Energy Agency (International Atomic Energy Agency 2014). They were placed at four different locations covering an elevations gradient of 1750 m and emptied on a monthly basis from April to November 2014 and 2015. Only the precipitation collector at the mountain hut Schaubach remained during winter 2014/2015 to collect winter precipitation. Due to limited accessibility mainly in spring and autumn, the collector was emptied after more than one month. Snow samples were derived from snow profiles as integrated and layer-specific samples, which were dug along an elevation gradient once a month from January to April 2015 and after snowfall events in August to October 2015.

EC was measured in the field by a portable conductivity meter WTW 3410 (WTW GmbH, Germany) with a precision of +/- 0.1 µS cm^{-1} (nonlinearly corrected by temperature compensation at 25 °C).

All samples were stored in 50 ml PVC bottles with a double cap and no headspace. The samples were kept in the dark at 4°C in the fridge before the analysis. δ^2H and $\delta^{18}O$ isotopic composition of all water samples (except the ISCO stream water samples at the outlet) were analysed at the Laboratory of Isotope and Forest Hydrology of the University of Padova (Italy), Department of Land, Environments, Agriculture and Forestry by an off-axis integrated cavity output spectroscope (model DLT-100 908-0008, Los Gatos Research Inc., USA). The analysis protocol and the description of reducing the carry-over effect are reported in (Penna et al., 2010, 2012). The instrumental precision (as an average standard deviation of 2094 samples) is 0.5‰ for δ^2H and 0.08‰ for $\delta^{18}O$.

The $\delta^{18}O$ isotopic composition of the ISCO stream water samples was analysed by an isotopic ratio mass spectrometer (GasBenchDelta V, Thermo Fisher) at the Free University of Bozen-Bolzano. Following the gas equilibration method (Epstein and Mayeda, 1953), 200-µl sub-samples were equilibrated with He–CO_2 gas at 23 °C for 18 h and then injected into the analyser. The isotopic composition of each sample was calculated from two repetitions, and the standard deviation was computed. The instrumental precision for $\delta^{18}O$ was ±0.2‰. We

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applied a correction factor, described in Engel et al. (2016), to adjust the isotopic compositions of $\delta^{18}O$ measured by the mass spectrometer to the ones measured by the laser spectroscope.

The analysis of major, minor and trace elements (Li, B, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Mo, Ba, Pb and U) was carried out by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS ICAP-Q, Thermo Fischer) at the laboratory of EcoResearch srl. (Bozen-Bolzano).

2.4 Data analysis

In order to better understand the effect of meteorological controls at different time scales, in particular precipitation and melting rates, different environmental variables derived from precipitation, air temperature, solar radiation and snow depth data from AWS Madritsch, were calculated (Table 3). Then, a sensitivity analysis was performed, which was based on a 1 day incremental time step and a temporal length of 30 days to respect the period of time between the monthly stream water samplings. As precipitation indicators, we considered the cumulated precipitation P in a period between 1 and 30 days prior to the sampling day, and the period of time D_{prec} in days starting from 1, 10 or 20 mm of cumulated precipitation occurred prior to the sampling day. As snow and ice melt indicators, we selected the maximum air temperature T_{max} and maximum global solar radiation G_{max} in a period between 1 and 30 days prior the sampling day. Moreover, we calculated the difference of snow depth ΔSD measured at the sampling day and the previous days, varying from 1 to 30 days. The temporal sensitivities of agreement between nivo-meteorological indicators and tracer signatures were expressed as Pearson correlation coefficients ($p < 0.5$) and represented a measure to obtain the most relevant nivo-meteorological indicators.

In order to understand the link among water sources and their hydrochemical composition, a principle component analysis (PCA), using data centred to null and scaled to variance one (R core team, 2016), was performed. Data below detection limit were excluded from the analysis.

To assess the dampening effect of meltwater on stream water chemistry during baseflow conditions and the melting period, the variability coefficient (VC) was calculated following Eq. (1):

$$\text{Variability coefficient VC} = SD_{baseflow}/SD_{melting} \qquad (1)$$

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$SD_{baseflow}$ is the standard deviation of stream EC sampled during baseflow conditions in winter at a given location and $SD_{melting}$ is the one at the same locations during the melt period in summer (following Sprenger et al., 2016).

A two-component hydrograph separation (HS) based on EC and δ^2H was assigned to separate the runoff contributions originating from the Sulden and Trafoi sub-catchment at each sampling moment during monthly sampling (Sklash and Farvolden, 1979), following Eq. (2) and Eq. (3):

$$Q_{S1} = Q_{S2} + Q_{T1} \qquad (2)$$

$$P_{T1} = (C_{S2} – C_{S1})/(C_{S2} – C_{T1}) \qquad (3)$$

where P is the runoff proportion, C is the electrical conductivity EC or isotopic composition in ^2H measured at the locations S1 (outlet), S2 (sampling location in the Sulden sub-catchment upstream the confluence with Trafoi River), and T1 (sampling location in the Trafoi sub-catchment upstream the confluence with Sulden River). While T1 served as ”old water” component, S2 represented the “new water” component at S1. The uncertainty in the two-component HS was expressed as Gaussian error propagation using the instrumental precision of the conductivity meter (0.1 µS cm^{-1}) and sample standard deviation from the laser spectroscope, following Genereux (1998). Furthermore, statistical analysis were performed to test the variance of hydrochemical data by means of a t-test (if data followed normal distribution), otherwise the nonparametric Mann-Whitney test was used.

3 Results

3.1 Origin of water sources

The isotopic signature of all water samples collected in the study area is shown in Fig. 2. Based on the isotopic signature of precipitation samples, the Local Meteoric Water Line (LMWL) was close to the Global Meteoric Water Line (GMWL). The isotopic signature of the other water sources fell on the water line, indicating that they originated from the same water vapour source as precipitation, with no or negligible secondary post-depositional fractionation. In more detail, rainfall samples represented the most enriched water source in the catchment (δ^2H: -128.6 to -15.14 ‰) while snow was the most depleted one (δ^2H: -196.3 to -86.7 ‰) and became more enriched through melting processes, with a smaller isotopic variability (δ^2H: -137.33 to -88.0 ‰). In contrast, glacier melt and rock glacier spring water were isotopically relatively similar and slightly more positive than snowmelt (δ^2H: -105.7 to -82.2 ‰, and -113.9 to -90.6 ‰, respectively). The isotopic range of spring water from the valley bottom (TSPR1-2, SSPR1) was relatively similar to the one of snowmelt (δ^2H: -105.7 to -88.8 ‰), with slightly more enriched samples from the Trafoi sub-catchment than from the Sulden sub-catchment. Only few water samples (i.e. snowmelt samples) plotted below the LMWL likely as a result of kinetic, non-equilibrium isotopic fractionation during the snowpack melting process (inset of Fig. 2).

To identify the geographic origin of stream water within the catchment, element concentrations of stream and rock glacier spring water are presented in Table 4 and 5. It is worth highlighting that heavy metal concentrations (such as Al, V, Cr, Ni, Zn, Cd, Pb) showed highest concentrations during intense melting in July 2015 at all six locations (partly exceeding concentration thresholds for drinking water (see European Union (Drinking Water) Regulations 2014). Element concentrations were clearly higher at the most upstream sampling locations. Relatively low variability coefficients (VC < 0.3) for these elements confirmed that larger variations of concentrations occurred during the melting period and not during baseflow conditions. Interestingly, the highest heavy metal concentrations (such as Mn, Fe, Cu, Pb) of rock glaciers springs SPR2 – 4 delayed the heavy metal concentration peak in the stream by about two months.

In contrast, other element concentrations (such as As, Sr, K, Sb) generally revealed higher concentrations during baseflow conditions and lower concentrations during the melting period. This observation was corroborated by relatively high variability coefficients for As (VC: 2 – 2.9) and Sb (VC: 2 – 2.2) at S1, S2, and T1. For example, while highest Sr concentrations were measured at S6, As was highest at the downstream locations T1, S2, and S1. Regarding the rock glacier springs, their hydrochemistry showed a gradual decrease in As and Sr concentration from July to September 2015. The observed geochemical patterns are confirmed by PCA results (Fig. 3) and the correlation matrix (Fig. 4), revealing that geochemical dynamics are driven by temporal (PC1) and spatial controls (PC2) and a typical clustering of elements, respectively. PC1 shows high loadings for heavy metal concentrations (such as Al, V, Cr, Ni, Zn, Cd, Pb), supporting the clear temporal dependency for the entire catchment (baseflow conditions vs. melting period)(Fig. 3a). PC2 is instead mostly characterized by high loadings of δ^2H and δ^{18}O in the Trafoi sub-catchment (i.e. T1 and TT2) and geochemical characteristics (EC, Ca, K, As and Sr) from the upstream region of the

Sulden River and rock glacier spring water (i.e. S6 and SSPR2-4, respectively). Overall, temporal and spatial controls explained a variance of about 53 %.

3.2 Temporal and spatial tracer variability

The temporal and spatial variability of EC in the Sulden and Trafoi River along the different sections, their tributaries, and springs is illustrated in Fig. 5. Results highlight the dominant impact of water enriched in solutes during baseflow conditions starting from late autumn to early spring prior to the onset of the melting period. Such an impact seemed to be highest in water from streams and tributaries reaching the most increased conductivity at S6, ranging from 967 to 992 µS cm^{-1} in January to March 2015. During the same period of time, isotopic composition was slightly more enriched and spatially more homogeneous among the stream, tributaries, and springs than in the summer months. In contrast, during the melting period, water from all sites in both sub-catchments became diluted due to different inputs of meltwater (Fig. 5 a, b), while water was most depleted during snowmelt dominated periods and less depleted during glacier melt dominated periods (Fig. 5c and 5d). Rainfall became a dominant runoff component during intense storm events. For instance, on 24 September 2015, a storm of 35 mm d^{-1} resulted in the strongest isotopic enrichment of this study, which is visible in Fig. 5c at T3 and TT2 (δ^2H -86.9 ‰; δ^{18}O: -12.4 ‰).

Hereinafter, the hydrochemistry of the Sulden and Trafoi sub-catchment is analyzed in terms of hydrochemical patterns of the main stream, tributaries, springs, and runoff contributions at the most downstream sampling location above the confluence. At T1 and S2, hydrochemistry was statistically different in its isotopic composition (Mann-Whitney Rank Sum Test: $p < 0.001$) but not in EC (Mann-Whitney Rank Sum Test: $p = 0.835$). Runoff originating from Trafoi and derived from the two-component HS, contributed to the outlet by about 36 % (±0.004) to 58 % (±0.003) when using EC and ranged from 29 % (±0.09) to 83 % (±0.15) when using δ^2H. Thus, runoff at the outlet was sustained more strongly by the Trafoi River during non-melting periods while the runoff from the Sulden sub-catchment dominated during the melting period.

By the aid of both tracers, catchment specific hydrochemical characteristics such as contrasting EC gradients along the stream were revealed (Fig. 5 and Fig. 6). EC in the Trafoi

River showed linearly increasing EC with increasing catchment area (from T3 to T1) during baseflow and melting periods ('EC enrichment gradient').

In contrast, the Sulden River revealed relatively high EC at the highest upstream location (S6) and relatively low EC upstream the confluence with the Trafoi River (S2) during baseflow conditions. The exponential decrease in EC ('EC dilution gradient') during this period of time was strongly linked to the catchment area. Surprisingly, the EC dilution along the Sulden River was still persistent during melting periods but highly reduced. In this context, it is also interesting to compare the EC variability (expressed as VC) along Trafoi and Sulden River during baseflow conditions and melting periods (Table 6). For both streams, VC increased with decreasing distance to the confluence (Trafoi River) and the outlet (Sulden River), and thus representing an increase in catchment size. The highest EC variability among all stream sampling locations is given by the lowest VC, which was calculated for S6. This location represents the closest one to the glacier terminus and showed a pronounced contrast of EC during baseflow conditions and melting periods (see Fig. 5 and Fig. 6).

Regarding the hydrochemical characterisation of the tributaries in both sub-catchments (Fig. 5), Sulden tributaries were characterised by a relatively low EC variability (68.2 – 192.3 µS cm^{-1}) and more negative isotopic values (δ^2H: -100.8 – 114.5 ‰) compared to the higher variability in hydrochemistry of the Sulden River. In contrast, the tracer patterns of Trafoi tributaries were generally consistent with the ones from the stream. Generally, also spring water at TSPR1, TSPR2, and SSPR1 followed these patterns during baseflow and melting periods in a less pronounced way, possibly highlighting the impact of infiltrating snowmelt into the ground. Comparing both springs sampled in the Trafoi sub-catchment indicated that spring waters were statistically different only when using EC (Mann-Whitney Rank Sum Test: $p = 0.039$). While TSPR1 hydrochemistry was slightly more constant, the one of TSPR2 was more variable from June to August 2015 (Fig. 5). This may result from different flow paths and disconnected recharge areas sustaining separately each spring, possibly pointing to a deeper (for TSPR1) and a shallower (for TSPR2) groundwater body.

3.3 Temporal variability at the catchment outlet

The temporal variability of the hydrochemical variables observed at the catchment outlet and of the meteorological drivers is illustrated in Fig. 7. Controlled by increasing radiation inputs and air temperatures above about 5°C in early summer (Fig. 7a and 7b), first snowmelt (as

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indicated by a depleted isotopic signature of about -14.6 ‰ in $\delta^{18}O$ and EC of about 200 µS cm^{-1}) induced runoff peaks in the Sulden River of about 20 m³ s^{-1} (starting from a winter baseflow of about 1.8 m^3 s^{-1}), as shown in Fig. 7c and 7e. Later in the summer, glacier melt induced runoff peaks reached about 13 – 18 m³ s^{-1}, which are characterised by relatively low EC (about 235 µS cm^{-1}) and isotopically more enriched stream water ($\delta^{18}O$: about -13.3 ‰). The highest discharge measured during the analysed period (81 m³ s^{-1} on 13 August 2014) was caused by a storm event, characterized by about 31 mm of precipitation falling over 3 hours at AWS Madritsch. Unfortunately, isotopic data for this event were not available due to a technical problem with the automatic sampler.

Water turbidity was highly variable at the outlet, and mirrored the discharge fluctuations induced by meltwater or storm events. Winter low flows are characterised by very low turbidity (< 10 NTU, corresponding to less than 6 mg l^{-1}). In summer, turbidity ranged between 20 and up to 1200 NTU during cold spells and melt events combined with storms, respectively. However, the maximum value recorded was 1904 NTU reached after several storm events of different precipitation amounts (17 mm, 50 mm, and 9 mm) on 12, 13, and 14 August 2014, respectively. Unfortunately, the turbidimeter did not work properly after the August 2014 flood peak, in mid-July 2015 and beginning of October 2015.

Furthermore, the interannual variability of meteorological conditions with respect to the occurrence of warm days, storm events and snow cover of the contrasting years 2014 and 2015 is clearly visible and contributed to the hydrochemical dynamics (Fig.7 and Table 1). While about 250 cm of maximal snowpack depth in 2014 lasted until mid-July, only about 100 cm were measured one year after with complete disappearance of snow one month earlier. In 2015, several periods of remarkable warm days occurred reaching more than 15°C at 2825 m a.s.l. and led to a catchment entirely under melting conditions (freezing level above 5000 m a.s.l., assuming a lapse rate of 6.5 K km^{-1}). In contrast, warmer days in 2014 were less pronounced and frequent but accompanied by intense storms of up to 50 mm d^{-1}. These meteorological conditions seem to contribute to the general hydrochemical patterns described above. Despite a relatively similar hydrograph with same discharge magnitudes during melt-induced runoff events in both years, EC and $\delta^{18}O$ clearly characterized snowmelt and glacier melt-induced runoff events in 2014. However, a characteristic period of depleted or enriched isotopic signature was lacking in 2015 so that snowmelt and glacier melt-induced runoff events were graphically more difficult to distinguish.

The daily variations in air temperature, discharge, turbidity, and EC showed marked differences in the peak timing. Maximum daily air temperature generally occurred between 12:00 and 15:00, resulting in discharge peaks at about 22:00 to 1:00 in early summer and at about 16:00 to 19:00 during late summer. Turbidity peaks were measured at 22:00 to 23:00 in May to June and clearly anticipated to 16:00 to 19:00 in July and August. In contrast, EC maximum occurred shortly after the discharge peak between 00:00 to 1:00 in early summer and at 11:00 to 15:00, clearly anticipating the discharge peaks.

It is interesting to highlight a complex hydrochemical dynamics during the baseflow period in November 2015, which was interrupted only by a rain-on-snow event on 28 and 29 October 2015. This events was characterized by more liquid (12.9 mm) than solid precipitation (6.6 mm) falling on a snowpack of about 10 cm (at 2825 m a.s.l.). While stream discharge showed a typical receding hydrograph confirmed by EC being close to the background value of about 350 µS cm^{-1}, $\delta^{18}O$ indicated a gradual isotopic depletion suggesting the occurrence of depleted water (e.g., snowmelt) in the stream. Indeed, also turbidity was more variable and slightly increased during this period.

To better characterize the temporal dynamics of hydrochemical variables, Fig. 8 shows the different relationships of discharge, EC, $\delta^{18}O$, and turbidity grouped for different months. In general, high turbidity seemed to be linearly correlated with discharge showing a monthly trend (Fig. 8a). In fact, this observation could be explained by generally higher discharges during melting periods (June, July, and August) and lower ones during baseflow conditions. Discharge and EC exhibited a relationship characterised by a hysteretic-like pattern at the monthly scale (Fig. 8b), which seemed to be associated with the monthly increasing contribution of meltwater with lower EC during melting periods contrasting with dominant groundwater contributions having higher EC during baseflow conditions.

During these periods, $\delta^{18}O$ of stream water was mainly controlled by the dominant runoff components (i.e. snowmelt and glacier melt in early summer and mid- to late summer, respectively) rather than the amount of discharge (Fig. 8c). Similarly, the relationship between $\delta^{18}O$ and EC was driven by the discharge variability resulting in a specific range of EC values for each month and by the meltwater component generally dominant during that period (Fig. 8d). As $\delta^{18}O$ was dependent on the dominant runoff components and less on the amount of discharge, turbidity showed no clear relationship with the isotopic composition

(Fig. 8e). In contrast, EC and turbidity were controlled by monthly discharge variations so that both variables followed the monthly trend, revealing a linear relationship (Fig. 8f).

3.4 Meteorological controls on hydrochemical stream responses within the catchment

To identify the most significant correlations between stream hydrochemistry (δ^2H and EC) and nivo-meteorological indicators (Table 3), the Pearson correlation coefficient was used. While significant correlations were generally found for maximum air temperature T_{max} (only for EC), maximum global solar radiation G_{max}, and the difference of snow depth ΔSD, other indicators such as cumulated precipitation P_{cum} and D_{Prec} were not significant (p < 0.05) and thus excluded from further analysis.

As the correlation of the most relevant nivo-meteorological indicators T_{max}, G_{max}, and ΔSD may vary depending on specific lag times, results from the sensitivity analysis are shown in Fig. 9. In general, ΔSD showed the highest positive correlations with tracers and were most sensitive for lag time of 1d, 5d, and 15d (Pearson correlation coefficient: 0.77, 0.63, and 0.85, respectively; p < 0.05). Furthermore, regarding global solar radiation and maximum air temperature, G_{max1d} and T_{max3d} showed best agreements (Pearson correlation coefficient: -0.83 and -0.7, respectively; p < 0.05).

To explore possible relationships between stream hydrochemistry (δ^2H and EC) and nivo-meteorological controls, selected indicators (at their most significant temporal scale) T_{max3d}, G_{max1d} and ΔSD_{15d} are shown in Fig.10 and 11. Those indicators represented the main drivers of EC and δ^2H variability within the Sulden and Trafoi catchment.

First, we observed that with increasing maximum air temperature T_{max3d}, EC concentration clearly decreased, strongly influenced by the dilution effect of meltwater. For example, an increase of T_{max3d} by 5°C (from 0° to 5°C) led to a decrease in EC in the Sulden and Trafoi River by about 15 – 154 µS cm^{-1} while a change from 10° to 15°C resulted in a drop of EC of about 22 – 225 µS cm^{-1} (Fig. 10a and b). Therefore, it can be noticed that the decrease in EC was highest with relatively high T_{max3d}. Interestingly, the dilution seemed to depend also on the sampling location along the stream and type of stream, as revealed by S6 (highest changes in EC) and ST2 (lowest changes in EC) locations in the Sulden sub-catchment.

Secondly, we analysed the relationship of EC concentration and global solar radiation. As shown in Fig. 10c to Fig. 10f, increasing maximum global solar radiation during the sampling

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day G_{max1d} (from 1400 to 1600 W m^{-2}) in the Sulden and Trafoi River led to strongly decreased EC concentrations by about 94 – 382 µS cm^{-1}. In agreement with T_{max3d}, the highest dilution effect was observed at S6. An isotopic depletion in δ^2H of 2.9‰ was calculated for the Sulden River, while it notably was 7.1‰ for the Trafoi River.

Finally, we could explain the dilution effect also by the negative changes of snow depth ΔSD, which represented the most sensitive variable to the temporal length (1d, 5d, and 15d) compared to the other variables (Fig. 9). Using the example of ΔSD_{15d} (measured at the sampling day and 15 days prior to the sampling day), EC concentrations in both sub-catchments resulted in less than 158 and 180 µS cm^{-1} when losses of snow depths were about 50 to 70 cm (Trafoi and S1 – S4 streams, respectively). Smaller losses from 10 to 20 cm were accompanied by still relatively high EC values of 256 and 301 µS cm^{-1} (Trafoi and S1 – S4 streams, respectively) but led to a drop in EC concentrations by about 35 to 42 µS cm^{-1} in both sub-catchments. Therefore, the decrease in EC was highest with relatively high ΔSD_{15d}.

With respect to δ^2H, the dilution effect was associated with the typical isotopic depletion of stream water, confirming the stream water dilution due to snowmelt input. On the one hand, changes in snow depth from 60 to 50 cm of snow depth resulted in a depletion of 2.36 ‰ to 2.79 ‰ and 2.24 to 2.59 ‰ in δ^2H at Trafoi and Sulden (S1, S2, S5) streams, respectively. On the other hand, changes of snow depth of less than 20 cm led only to smaller isotopic depletion of 1.05 to 1.19 ‰ for the Trafoi and Sulden River. Not surprisingly, the clear linear relationship between ΔSD and tracers held only for losses in snow depth. In contrast, positive changes in ΔSD led to remarkably higher variability in EC and δ^2H in the river network.

4 Discussion

4.1 Comparison of meteoric water lines

The geographic origin of water vapour can generally be inferred by comparing the LMWL to the GMWL (Craig 1961). Study results showed that precipitation was mainly formed by water vapour originated from the Atlantic Ocean, which was in general agreement with the findings of other studies. The LMWL of the Sulden catchment was very similar to the one from a station at 2731 m a.s.l. in the Vermigliana Valley (δ^2H (‰)=8 δ^{18}O + 7.8) (Chiogna et al., 2014) and a station at 2300 m a.s.l. in the Noce Bianco catchment (δ^2H (‰)=7.5 δ^{18}O + 7.9;

R^2 = 0.97, n=40) (Carturan et al., 2016), located south between the Ortles-Cevedale and Adamello–Presanella group. However, it was slightly different in terms of d-excess when considering the LMWL of Matsch/Mazia Valley (d-excess: 10.3, Penna et al., 2014) and Northern Italy (d-excess: 9.4, Longinelli and Selmo, 2003). Moreover, it clearly differed from the Mediterranean Meteoric Water Line (MMWL: δ^2H (‰) = 8 $\delta^{18}O$ + 22; Gat and Carmi, 1970). These observations may confirm the presence of different precipitation patterns and microclimates at the regional scale (Brugnara et al., 2012).

4.2 Geological controls and hydrological connectivity

Geochemical dynamics were driven by a pronounced release of heavy metals (such as Al, V, Cr, Ni, Zn, Cd, Pb) shown for the entire catchment and, in contrast, by a specific release of As and Sr in the upper and lower Sulden sub-catchment (Fig. 3). Yet, as the explained variance was only at about 53 %, further controls may be present. In this context, PC3 explained 11.8 % of additional variance and may represent surface vs. subsurface flows or residence time within the soil.

With respect to the first observation, several sources of heavy metals can be addressed: on the one hand, these elements may be released by rock weathering on freshly-exposed mineral surfaces and sulphide oxidation, typically produced in metamorphic environments (Nordstrom et al., 2011). Proglacial stream hydrochemistry may also strongly depend on the seasonal evolution of the subglacial drainage system that contribute to specific element releases (Brown and Fuge, 1998). In this context, rock glacier thawing may play an important role for the release of Ni (Thies et al., 2007; Mair et al., 2011; Krainer et al., 2015) and Al and Mn (Thies et al., 2013). However, high Ni concentrations were not observed in this study. Moreover, high heavy metal concentrations were measured during the melting period in mid-summer, which would generally be too early to derive from permafrost thawing (Williams et al., 2006; Krainer et al., 2015). Also bedrock weathering as major origin probably needs to be excluded because low concentrations occurred in winter when the hydrological connectivity at higher elevations was still present (inferred from running stream water at the most upstream locations).

On the other hand, it is therefore more likely that heavy metals derive from meltwater itself due to the spatial and temporal dynamics observed. This would suggest that the element release is strongly coupled with melting and infiltration processes, when hydrological

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connectivity within the catchment is expected to be highest. To support this explanation, supplementary element analysis of selected snowmelt (n = 2) and glacier melt (n = 2) samples of this study were conducted. Although these samples did not contain high concentrations of Cd, Ni, and Pb, for example, snowmelt in contact with the soil surface was more enriched in such elements than dripping snowmelt. Moreover, snowmelt and ice melt samples from the neighbouring Matsch/Mazia Valley in 2015 were strongly controlled by high Al, Co, Cd, Ni, Pb and Zn concentrations (Engel et al., 2017). As shown for 21 sites in the Eastern Italian Alps (Veneto and Trentino-South Tyrol region), hydrochemistry of the snowpack can largely be affected by heavy metals originating from atmospheric deposition from traffic and industry (such as V, Sb, Zn, Cd, Mo, and Pb) (Gabrielli et al., 2006). Likely, orographically induced winds and turbulences arising in the Alpine valleys may often lead to transport and mixing of trace elements during winter. Studies from other regions, such as Western Siberia Lowland and the Tibetan Plateau, agree on the anthropogenic origin (Shevchenko et al., 2016 and Guo et al., 2017, respectively).

In contrast, with respect to the origin of As and Sr, a clear geological source can be attributed, supporting the first hypothesis on bedrock-specific geochemical signatures. In the lower Sulden catchment (i.e. S1, S2, and T1), As could mainly originate from As-containing bedrocks. As rich lenses are present in the cataclastic carbonatic rocks (realgar bearing) and in the mineralized, arsenopyrite bearing bands of quartzphyllites, micaschists and paragneisses of the crystalline basement. Different outcrops and several historical mining sites are known and described in the literature (Mair, 1996, Mair et al., 2002, 2009; Stingl and Mair, 2005). In the upper Sulden catchment, the presence of As is supported by the hydrochemistry of rock glacier outflows in the Zay sub-catchment (corresponding to the drainage area of ST2; Engel et al., 2018) but was not reported in other studies (Thies et al., 2007; Mair et al., 2011; Krainer et al., 2015; Thies et al., 2013). Also high-elevation spring waters in the Matsch Valley corroborated that As and Sr concentrations may originate from paragneisses and micaschists (Engel et al., 2017). In this context, we suggest a controlling mechanism as follows: the gradual decrease in As and Sr concentrations from rock glacier springs clearly disagrees with the observations from other studies that rock glacier thawing in late summer leads to increasing element releases (Williams et al., 2006; Thies et al., 2007; Krainer et al., 2015; Nickus et al., 2015). Therefore, it is more likely that As and Sr originate from the Quarzphyllite rocks, that form the bedrock of the rock glaciers (see Andreatta, 1952;

Montrasio et al., 2012). Weathering and former subglacial abrasion facilitate the release (Brown, 2002). As- and Sr-rich waters may form during winter when few quantities of water percolate in bedrock faults and then are released due to meltwater infiltration during summer (V. Mair, personal communication, 2018). As a clear delayed response of heavy metal concentrations in rock glacier outflow was revealed, the infiltration and outflow processes along flow paths in the bedrock near the rock glaciers may take up to two months to hydrochemically respond to snowmelt contamination.

As a consequence, a clear hydrochemical signature of permafrost thawing is difficult to find and results may lack the transferability to other catchments as not all rock glaciers contain specific elements to trace (Colombo et al., 2017). In this context, as precipitation and snowmelt affect the water budget of rock glaciers (Krainer and Mostler, 2002; Krainer et al., 2007), potential impacts of atmospheric inputs on rock glacier hydrochemistry could be assumed and would deserve more attention in future (Colombo et al., 2017).

Furthermore, export of elements in fluvial systems is complex and may strongly be affected by the pH (Nickus et al., 2015) or interaction with solids in suspension (Brown et al., 1996), which could not be addressed in this study. Further insights on catchment processes might be gained considering also element analysis of the solid fraction, to investigate whether water and suspended sediment share the same provenance.

4.3 The role of nivo-meteorological conditions and topography

Superimposing the impact of the geological origin, melting processes were controlled by meteorological conditions and topography, affecting stream hydrochemistry during summer, as shown by isotope dynamics (Fig. 5 and 7) and hydrochemical relationships (Fig. 8). It is well known that high correlations between snow or glacier melt and maximum air temperature exist (U.S. Army Corps of Engineers 1956; Braithwaite 1981), thus controlling daily meltwater contributions to streamflow (Mutzner et al., 2015; Engel et al., 2016). While ΔSD was used in this study, also snow depth and the extent of snow cover are suggested as effective indicators, exhibiting a strong control on runoff dynamics and thus melting processes (Singh et al., 2005). Likely, more specific explanatory variables such as vapour pressure, net radiation, and wind (Zuzel and Cox, 1975) or turbulent heat fluxes and long-wave radiation (Sicart et al., 2006) may exist but were not included in the present study due to the lack of observations.

As shown in this study, dilutions effects and isotopic depletion could rather be explained by maximum values T_{max3d} and G_{max1d} than averages of nivo-meteorological indicators or precipitation-related indicators. This result confirms the second hypothesis on the importance of nivo-meteorological indicators controlling melt processes by radiation and air temperature. Such observation may imply the importance of threshold-like controls at the daily and short-term scale, leading to tipping points along the cascade from atmospheric circulation and local climate to hydrology to physico-chemical habitat (Milner et al., 2009). In this regard, the (cumulated) daily maximum positive air temperature was used to characterize the decay of simulated snow albedo related to snow metamorphism (Ragettli and Pellicciotti, 2012). The authors also defined a threshold temperature for melt onset of 5°C, being in agreement with our findings (shown in Fig. 7, Fig. 10a, and Fig. 10b). Moreover, relatively small changes and low indicator values led to hydrochemical changes in stream water composition. This could be justified by the fact that nivo-meteorological indicators were derived from 2825 m a.s.l., meaning that only about 30 % of the catchment area (assuming elevation bands of 50 m) were above this location. Therefore, meteorological conditions and related nivo-meteorological indicator may be more sensitive when compared to hydrochemical responses of the entire catchment. While favourable melting conditions are certainly delayed at higher elevations, stream water composition detected along the Sulden and Trafoi River (except S6 being closest to the weather station) would mainly reflect melting processes originating from the lower reaches within the catchment.

In this study, the most pronounced dilution effect and isotopic depletion (regarding monthly data) could be attributed to G_{max1d}, which thus may be considered as the most relevant nivo-meteorological indicator. This observation could be supported by Vincent and Six (2013), who found that spatial variations of ice ablation were mainly driven by potential solar radiation. It is further considered to be the main energy source driving melt processes in glacierized catchments of different climates (Sicart et al., 2008) and may integrate the effect of cloud coverage (Anslow et al., 2008). In contrast, lower radiation inputs and subzero air temperatures occurred during snowfall events (indicated by positive ΔSD) and likely interrupted melt processes, leading to higher variability of hydrochemical stream water composition (Hannah et al., 1999; Sicart et al., 2006; DeBeer and Pomeroy, 2010).

Results from the temporal sensitivity analysis are generally difficult to compare due to the lack of suitable studies and thus provide a novel data set for glacierized catchments. The sensitivity of ΔSD to different temporal length (3d, 5d, 15d) may indicate potential meltwater storage components and their effectiveness to route meltwater at different temporal scales. First, the snowpack represents a short-term storage for meltwater ranging from few hours to few days (Coléou and Lesaffre, 1998), due to different snowpack properties (i.e. irreducible water saturation, layer thickness) (Colbeck 1972; Marsh and Pomeroy, 1996). Second, the presence of slower and quicker flow paths within glacial till, talus, moraines, and shallow vs. deeper groundwater compartments could justify the intermediate (5d) and longer (15d) meltwater response (Brown et al., 2006; Roy and Hayashi, 2009; McClymont et al., 2010; Fischer et al., 2015; Weiler et al., 2017).

4.4 Implications for streamflow and hydrochemistry dynamics

Tracer dynamics of EC and stable isotopes associated with monthly discharge variations generally followed the conceptual model of the seasonal evolution of streamflow contributions, as described for catchments with glacierized area of 17 % (Penna et al. 2017) and 30 % (Schmieder et al. 2017). However, isotopic dynamics were generally less pronounced compared to these studies, likely resulting from the impact of relative meltwater contribution related to different catchment sizes and the proportion of glacierized area (Baraer et al., 2015).

In addition, hydrometric and geochemical dynamics analysed in this study were controlled by an interplay of meteorological conditions and the heterogeneity of geology. Such an interplay is highlighted by EC dynamics (i.e. EC variability derived from VC), to be further controlled by the contributing catchment area (i.e. EC gradients along the Sulden and Trafoi River). As EC was highly correlated to Ca concentration (Spearman rank correlation: 0.6, $p < 0.05$; see Fig. 4), EC dynamics were determined by the spatial distribution of different geology. For example, as dolomitic rocks are present almost within the entire Trafoi sub-catchment, meltwater following the hydraulic gradient can likely become more enriched in solutes with longer flow pathways and increasing storage capability related to the catchment size (Fig. 6). As consequence, the 'EC enrichment gradient' could persist during both the melting period and baseflow conditions in the presence of homogenous geology. Therefore, topography as control may become more important than the geological setting, to control spatial stream water variability. In the Sulden sub-catchment, however, dolomitic rocks are only present in the upper part of the catchment while metamorphic rocks mostly prevail. This leads to a

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pronounced dilution of Ca-rich waters with increasing catchment area or in other words, increasing distance from the source area (Fig. 6) during baseflow conditions. This implies that meltwater contributions to the stream homogenize the effect of geographic origin on different water sources, having the highest impact in vicinity to the meltwater source (see Table 6).

The additional effect of topographical characteristics is underlined by the findings that the Sulden River hydrochemistry at S2 was significantly more depleted in δ^2H and δ^{18}O than T1 hydrochemistry. Compared with the Sulden sub-catchment, the Trafoi sub-catchment has a slightly lower proportion of glacier extent but, more importantly, has a clearly smaller catchment area within the elevation bands of 1800 to 3200 m a.s.l. (i.e. 40.2 km² for the Trafoi and 66.5 km² for the Sulden sub-catchment). In this elevation range, the sub-catchments of major tributaries ST1, ST2, and ST3 are situated, which deliver large snowmelt contributions to the Sulden River (Fig. 6).

In consequence, resulting from the impact of these different controls, specific hydrometric and hydrochemical relationships derive. For example, the hysteretic relationship between discharge and EC (Fig. 8b) helps to identify the conditions with maximum discharge and EC: during baseflow conditions, the Sulden River showed highest EC of about 350 µS cm^{-1} seemingly to be bound to only about 3 m³ s^{-1} whereas the maximum dilution effect occurred during a storm on 29 June 2014 (55 mm of precipitation at AWS Madritsch) with 29.3 m³ s^{-1} of discharge resulting in only 209 µScm^{-1}. However, these observations based on daily data sampled at 23:00, likely not capturing the entire hydrochemical variability inherent of the Sulden catchment. As shown in Fig. 5 and Fig. 7, much higher discharges and thus even lower EC could be reached along the Sulden River and inversely, which was potentially limited by the specific geological setting of the study area.

As more extreme weather conditions (such as heat waves, less solid winter precipitation) are expected in future (Beniston, 2003; Viviroli et al., 2011; Beniston and Stoffel 2014), glacierized catchments may exhibit more pronounced hydrochemical responses such as shifted or broader ranges of hydrochemical relationships and increased heavy metal concentrations both during melting periods and baseflow conditions. However, identifying these relationships with changing meteorological conditions would deserve more attention and is strongly limited by our current understanding of underlying hydrological processes (Schaefli et al., 2007). In a changing cryosphere, more complex processes such as non-stationarity processes may emerge under changing climate, which itself was found to be a major cause of non-stationarity (Milly et al., 2008). In this context, explaining the hydrochemical dynamics ambiguity observed during the baseflow period in November 2015 (Fig. 7) will deserve further attention.

Finally, our results can partly confirm the third hypothesis following Heidbüchel et al. (2013). Long-term controls such as geology and topography govern hydrochemical responses at the spatial scale (such as bedrock-specific geochemical signatures, EC gradients, and relative snowmelt contribution). In contrast, short-term controls such as maximum daily solar radiation, air temperature, and snow depth differences drive short-term responses (such as discharge variability and EC dilution). However, as the catchment response strongly depended on the melting period vs. baseflow conditions, controls at longer temporal scales interact as well. Thus, our findings suggest that glacierized catchments react in a much more complex way and that catchment responses cannot be attributed to one specific scale, justified by either short-term or long-term controls alone.

In this context, the present study provides novel insights into geological, meteorological, and topographic controls of stream water hydrochemistry rarely addressed for glacierized catchments so far. Moreover, this study strongly capitalizes on an important dataset that combines nivo-meteorological indicators and different tracers (stable isotopes of water, EC, major, minor and trace elements), underlining the need for conducting multi-tracer studies in complex glacierized catchments.

4.5 Methodological limitation

The sampling approach combined a monthly spatial sampling with daily sampling at the outlet, which methodologically is in good agreement with other sampling approaches, accounting for increasing distance of sampling points to the glacier (Zhou et al., 2014; Baraer et al., 2015), intense spatial and temporal sampling (Penna et al., 2014; Fischer et al., 2015), synoptic sampling (Carey et al., 2013; Gordon et al., 2015), and different catchment structures such as nested catchments (Soulsby et al., 2006b). Sampling covered a variety of days with typical snowmelt, glacier melt and baseflow conditions during 2014 and 2015, confirming the representativeness of tracer dynamics within two years contrasting in their meteorological characteristics (Table 1). However, short-term catchment responses (such as storm-induced peak flows and related changes in hydrochemistry) were difficult to be captured by this sampling approach. Furthermore, two years of field data are probably not sufficient to capture all hydrological conditions and catchment responses to specific meteorological conditions. In this regards, long-term studies may have better chances in capturing the temporal variability of hydrochemical responses (Thies et al., 2007). In this context, sampling approaches might need to become more complex in future to unravel further process understanding of glacierized catchments.

5 Conclusions

Our results highlight the complex hydrochemical responses of mountain glacierized catchments at different temporal and spatial scales. To our knowledge, only few studies investigated the impact of controlling factors on stream water hydrochemistry by using nivo-meteorological indicators and multi-tracer data, which we recommend to establish as prerequisite for studies in other glacierized catchments.

The main results of this study can be summarized as follows:

- Hydrometric and geochemical dynamics were controlled by an interplay of meteorological conditions and the geological heterogeneity. The majority of the variance (PC1: 36.3 %) was explained by heavy metal concentrations (such as Al, V, Cr, Ni, Zn, Cd, Pb), associated with atmospheric deposition on the snowpack and release through snowmelt. Remaining variance (PC2: 16.3 %) resulted both from the presence of a bedrock-specific geochemical signature (As and Sr concentrations) and the role of snowmelt contribution.
- The isotopic composition of rock glacier outflow was relatively similar to the composition of glacier melt whereas high concentrations of As and Sr may more likely result from bedrock weathering.
- At the monthly scale for different sub-catchments (spatial scale: 0.05 – 130 km²), both $\delta^{18}O$ and EC revealed complex spatial and temporal dynamics such as contrasting EC gradients during baseflow conditions and melting periods.
- At the daily scale for the entire study area (spatial scale: 130 km²), we observed strong relationships of hydrochemical variables, with mainly discharge and EC exhibiting a strong monthly relationship. This was characterised by a hysteretic-like pattern, determined by highest EC and lowest discharge during baseflow conditions on the one hand and maximum EC dilution due to highest discharge during a summer storm.

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- Main drivers of EC and δ^2H variability were the nivo-meteorological indicators T_{max3d}, G_{max1d} and ΔSD_{15d}. ΔSD was found to be the most sensitive variable to different temporal lengths (3d, 5d, and 15d) and G_{max1d} resulted in the most pronounced EC dilution and isotopic depletion.

Finally, this study may support future classifications of glacierized catchments according to their hydrochemical response under different catchment conditions or the prediction of appropriate end-member signatures for hydrograph separation being valid at longer time scales.

6 Data availability

Hydrometeorological data are available upon request at the Hydrographic Office of the Autonomous Province of Bozen-Bolzano. Tracer data used in this study are freely available by contacting the authors.

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Table 1. Meteorological characteristics of the weather station Madritsch/Madriccio 2.825 m a.s.l. in 2014 and 2015.

Date	2014	2015
Precipitation (total / rain / snow) (mm y^{-1})*	1284/704/579	961/637/323
Mean annual air temperature (°C)	-1.4	-0.8
Days with snow cover > 10cm	270	222
Maximum snow depth (date)	02/03/2014	27/03/2015
Maximum snow depth (cm)	253	118
Date of snow cover disappearance	12/07/2014	13/06/2015
Average discharge (median) ($m^3 s^{-1}$)	9.5	5.2

* Precipitation data are not wind-corrected. Rain vs. snow separation was performed following Auer (1974)

1128 Table 2. Topographical characteristics of sub-catchments defined by sampling points.

Sampling point	Description	Catchment area (km²)	Glacier cover (%)	Elevation range
T1	Trafoi River	12.18	17	1197 - 3889
T2	Trafoi River	46.72	18.6	1404 - 3889
T3	Trafoi River	51.28	35	1587 - 3469
TT1	Tributary draining Trafoi glacier	4.32	27.1	1587 - 3430
TT2	Small creek	0.05	0	1607 - 2082
TT3	Tributary draining Zirkus/ Circo glacier	6.46	44	1605 - 3888
TSPR1	Spring at the foot of a slope	-	0	1602*
TSPR2	Spring at the foot of a slope	-	0	1601*
S1	Sulden River	130.14	13.6	1109 - 3896
S2	Sulden River	74.61	12.1	1296 - 3896
S3	Sulden River	57.01	15.8	1707 - 3896
S4	Sulden River	45.06	18.6	1838 - 3896
S5	Sulden River	18.91	29.7	1904 - 3896
S6	Sulden River	14.27	38.5	2225 - 3896
ST1	Razoi tributary	6.46	0.6	1619 - 3368
ST2	Zay tributary	11.1	12.8	1866 - 3543
ST3	Rosim tributary	7.3	9.7	1900 - 3542

SSPR1	Spring in the valley bottom near Sulden town	-	0	1841*
SSPR2 - 4	At the base of the rock glacier front	-	0.12**	2614, 2594, 2600*

* for spring locations, the elevation of the sampling point is given.

** for rock glacier spring locations, the glacier cover refers to the extent of both rock glaciers.

Table 3. Environmental variables derived from the weather station Madritsch/Madriccio at 2825 m a.s.l..

Variable	Unit	Description
P_{1d}	mm	Cumulated precipitation of the sampling day
P_{nd}		Cumulated precipitation n days prior to sampling day
T_{max1d}	°C	Maximum air temperature during the sampling day
T_{maxnd}		Maximum air temperature within n days prior to sampling day
G_{max1d}	W/m²	Maximum global solar radiation during sampling day
G_{maxnd}		Maximum global solar radiation within n days prior to sampling day
ΔSD_{1d}	cm	Difference of snow depth measured at the sampling day at 12:00 and the previous day at 12:00, based on 6h averaged snow depth records.
ΔSD_{nd}		Difference of snow depth measured at the sampling day at 12:00 and n days prior the sampling day at 12:00, based on 6h averaged snow depth records.
D_{Prec1}	days	Days since last daily cumulated precipitation of > 1mm was measured.
D_{Prec10}		Days since last daily cumulated precipitation of > 10mm was measured.
D_{Prec20}		Days since last daily cumulated precipitation of > 20mm was measured.

Table 4. Statistics of element concentration (in µg l^{-1}) from selected stream, tributary and active rock glacier springs in the Sulden catchment sampled from March to October 2015. CV: coefficient of variation. VC: variability coefficient (see Eq. 1) with $SD_{baseflow}$ (based on samples from March, April, and October 2015) and $SD_{melting}$ (based on samples from May to September 2015). Note that CV was not calculated for SSPR2 – 4 as water samples were available only during summer.

Location	Statistic	Na	Mg	Al	K	Ca	V	Cr	Mn	Fe	Ni	Cu
S1	min	1881.3	12169.1	6.9	1051.2	41497.2	0.2	0.2	1.1	21.1	0.5	1.5
	max	7246.9	19547.1	541.4	2456.0	56508.3	1.8	1.4	62.4	1038.9	3.8	9.1
	mean	3253.5	14625.4	148.7	1657.3	48423.7	0.6	0.6	15.0	292.5	1.3	4.9
	SD	1782.0	2265.3	157.3	487.1	4538.1	0.5	0.3	18.7	300.2	1.0	3.0
	CV	0.5	0.2	1.1	0.3	0.1	0.9	0.5	1.2	1.0	0.8	0.6
	VC	0.6	0.3	0.3	1.6	0.5	0.2	0.2	0.1	0.3	0.2	0.8
S2	min	1968.4	9793.3	6.1	1546.3	43167.9	0.1	0.2	1.1	12.0	0.3	1.3
	max	3334.6	16453.8	743.1	2476.3	73177.3	1.9	1.7	71.0	1513.5	3.8	9.1
	mean	2431.6	12437.2	211.2	1900.9	52361.7	0.6	0.6	18.5	410.7	1.2	3.3
	SD	409.4	2292.5	236.4	299.3	8738.1	0.6	0.5	22.4	467.9	1.1	2.4

	CV	0.2	0.2	1.1	0.2	0.2	1.0	0.8	1.2	1.1	0.9	0.7
	VC	2.0	0.2	0.2	0.7	0.2	0.1	0.2	0.1	0.2	0.2	0.2
S6	min	1262.6	17458.6	9.0	1042.6	67588.1	0.1	0.1	1.5	21.6	0.5	1.5
	max	2277.0	34928.5	799.4	1748.4	166731.5	3.4	1.9	104.6	1587.1	6.2	17.0
	mean	1805.6	22862.4	278.4	1362.7	129896.0	1.1	0.8	43.1	596.1	2.1	6.5
	SD	339.4	5512.9	321.0	259.4	28165.0	1.2	0.7	47.4	670.0	1.9	4.9
	CV	0.2	0.2	1.2	0.2	0.2	1.2	0.8	1.1	1.1	0.9	0.8
	VC	0.6	0.2	0.0	1.4	0.5	0.0	0.1	0.0	0.1	0.1	0.2
SSPR2-4	min	1768.3	10051.4	9.0	1236.1	76848.5	0.0	0.1	1.5	16.7	0.2	0.5
	max	2818.6	29509.5	321.2	2402.5	131149.7	2.5	0.6	71.7	492.2	1.5	38.3
	mean	2199.9	17254.4	68.9	2009.0	94611.4	0.4	0.3	13.1	127.5	0.7	8.2
	SD	343.3	6935.8	97.8	294.4	21508.4	0.8	0.2	22.5	148.5	0.5	11.7
	CV	0.2	0.4	1.4	0.1	0.2	2.2	0.5	1.7	1.2	0.7	1.4
T1	min	1125.7	13481.8	6.3	536.9	33044.0	0.2	0.1	0.9	13.3	0.3	0.4

	max	3312.9	42197.2	914.7	1470.6	88033.8	4.5	1.8	121.8	1178.5	3.5	22.0
	mean	2078.3	19230.5	139.8	985.9	48369.3	0.8	0.5	19.1	190.2	1.1	5.1
	SD	600.5	8846.6	293.5	302.7	16108.6	1.4	0.5	38.9	374.8	1.0	6.6
	CV	0.3	0.5	2.1	0.3	0.3	1.8	1.0	2.0	2.0	0.9	1.3
	VC	1.3	0.1	0.0	0.8	0.3	0.0	0.3	0.0	0.0	0.2	0.2
TT2	min	321.0	12048.8	4.7	272.8	23873.4	0.1	0.2	0.8	10.4	0.3	0.7
	max	2524.5	20756.5	568.0	1017.1	39335.1	2.0	1.3	57.1	1116.2	2.7	22.2
	mean	1148.1	16898.0	97.0	551.6	32228.7	0.4	0.4	10.2	173.2	0.9	8.0
	SD	727.9	2945.5	179.7	244.1	4615.5	0.6	0.4	17.9	357.5	0.7	7.7
	CV	0.6	0.2	1.9	0.4	0.1	1.5	0.9	1.8	2.1	0.8	1.0
	VC	0.9	0.8	0.1	0.6	0.5	0.1	0.3	0.1	0.1	0.3	0.2

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Table 5. Statistics of element concentration (in µg l^{-1}) from selected stream, tributary and active rock glacier springs in the Sulden catchment sampled from March to October 2015. CV: coefficient of variation. VC: variability coefficient (see Eq. 1) with $SD_{baseflow}$ (based on samples from March, April, and October 2015) and $SD_{melting}$ (based on samples from May to September 2015). Note that CV was not calculated for SSPR2 – 4 as water samples were available only during summer.

location	statistics	Zn	As	Se	Rb	Sr	Ag	Cd	Sb	Hg	Pb	U
S1	min	4.1	12.1	0.5	0.0	307.9	0.0	0.0	0.2	0.0	0.4	0.0
	max	23.2	61.1	1.1	2.6	390.5	0.1	0.1	0.5	0.2	7.6	11.3
	mean	9.7	27.0	0.8	1.1	349.8	0.0	0.1	0.3	0.1	2.1	5.1
	SD	5.8	15.5	0.2	1.1	27.2	0.0	0.1	0.1	0.1	2.3	5.2
	CV	0.6	0.6	0.2	1.0	0.1	2.6	1.0	0.4	1.1	1.1	1.0
	VC	0.2	2.6	1.0	0.0	0.7	-	1.0	2.0	0.0	0.1	0.0
S2	min	3.7	15.1	0.4	0.0	334.0	0.0	0.0	0.1	0.0	0.3	0.0
	max	23.8	40.9	0.7	3.4	609.9	0.0	0.1	0.2	0.2	9.4	11.3
	mean	8.5	23.3	0.5	1.6	410.7	0.0	0.0	0.2	0.1	2.7	4.9
	SD	6.4	8.0	0.1	1.6	81.0	0.0	0.0	0.0	0.1	3.4	5.1

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	CV	0.7	0.3	0.2	1.0	0.2	-	1.3	0.3	1.1	1.3	1.0
	VC	0.2	2.0	0.5	0.0	0.3	-	1.0	1.0	0.0	0.1	0.0
S6	min	5.6	6.3	0.5	0.0	524.0	0.0	0.0	0.3	0.0	0.4	0.0
	max	40.9	17.0	1.2	1.9	2024.0	0.0	0.2	0.5	0.1	18.1	11.3
	mean	19.1	10.1	0.9	0.7	1380.5	0.0	0.1	0.3	0.0	6.7	4.0
	SD	12.9	4.0	0.2	0.8	463.1	0.0	0.1	0.1	0.0	7.3	4.9
	CV	0.7	0.4	0.2	1.2	0.3	-	0.9	0.2	1.2	1.1	1.2
	VC	0.2	0.1	0.5	0.0	0.5	-	0.5	2.2	0.0	0.0	0.0
SSPR2-4	min	1.5	6.3	0.4	0.0	341.2	0.0	0.0	0.1	0.0	0.2	0.0
	max	49.4	38.0	0.6	2.7	1355.7	0.1	0.4	0.4	0.1	19.8	27.2
	mean	10.7	31.1	0.5	0.9	770.9	0.0	0.1	0.2	0.0	3.1	6.9
	SD	14.8	4.4	0.1	1.0	435.7	0.0	0.1	0.1	0.0	6.3	9.4
	CV	1.4	0.1	0.2	1.1	0.6	2.6	1.4	0.6	1.3	2.0	1.4

T1	min	2.3	7.2	0.6	0.0	220.9	0.0	0.0	0.2	0.0	0.3	0.0
	max	46.5	64.2	1.4	1.9	478.1	0.0	0.2	0.7	0.2	18.0	12.5
	mean	10.9	24.5	1.1	0.7	340.1	0.0	0.1	0.4	0.1	2.9	5.6
	SD	13.6	18.4	0.3	0.7	75.8	0.0	0.1	0.1	0.1	5.7	5.7
	CV	1.2	0.8	0.2	1.1	0.2	-	1.4	0.4	1.1	2.0	1.0
	VC	0.1	2.9	0.6	0.0	0.9	-	0.6	2.0	0.0	0.0	0.0
TT2	min	2.8	0.3	0.5	0.0	149.4	0.0	0.0	0.2	0.0	0.3	0.0
	max	39.4	1.2	1.5	1.7	384.5	0.5	0.1	0.5	0.7	9.1	10.6
	mean	9.9	0.7	1.0	0.4	247.5	0.1	0.0	0.3	0.1	1.8	4.8
	SD	11.4	0.3	0.3	0.5	67.5	0.2	0.0	0.1	0.2	2.8	4.9
	CV	1.2	0.4	0.3	1.5	0.3	2.6	1.3	0.4	1.8	1.5	1.0
	VC	0.1	0.3	1.3	0.0	1.2	0.0	1.0	-	0.0	0.1	0.0

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Table 6. Variability coefficient (VC) for selected locations along the Sulden and Trafoi River in 2014 and 2015.

Location	River section (in km)	VC
T3	6.529	0.70
T2	2.774	0.85
T1	51	1.09
S6	12.87	0.01
S3	6.417	0.42
S2	2.739	0.35
S1	0	0.77

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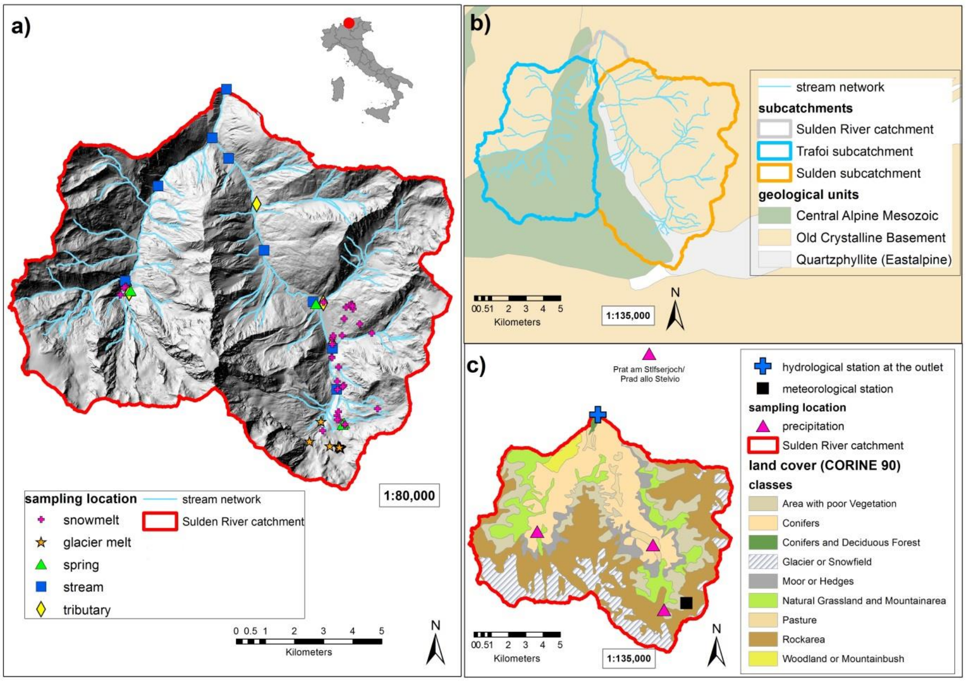

Figure 1. Overview of the Sulden catchment with a) sampling point, b) geology, and c) land cover with instrumentation. The meteorological station shown is the Madritsch/Madriccio AWS of the Hydrographic Office (Autonomous Province of Bozen-Bolzano). The glacier extent refers to 2006 (Autonomous Province of Bozen-Bolzano).

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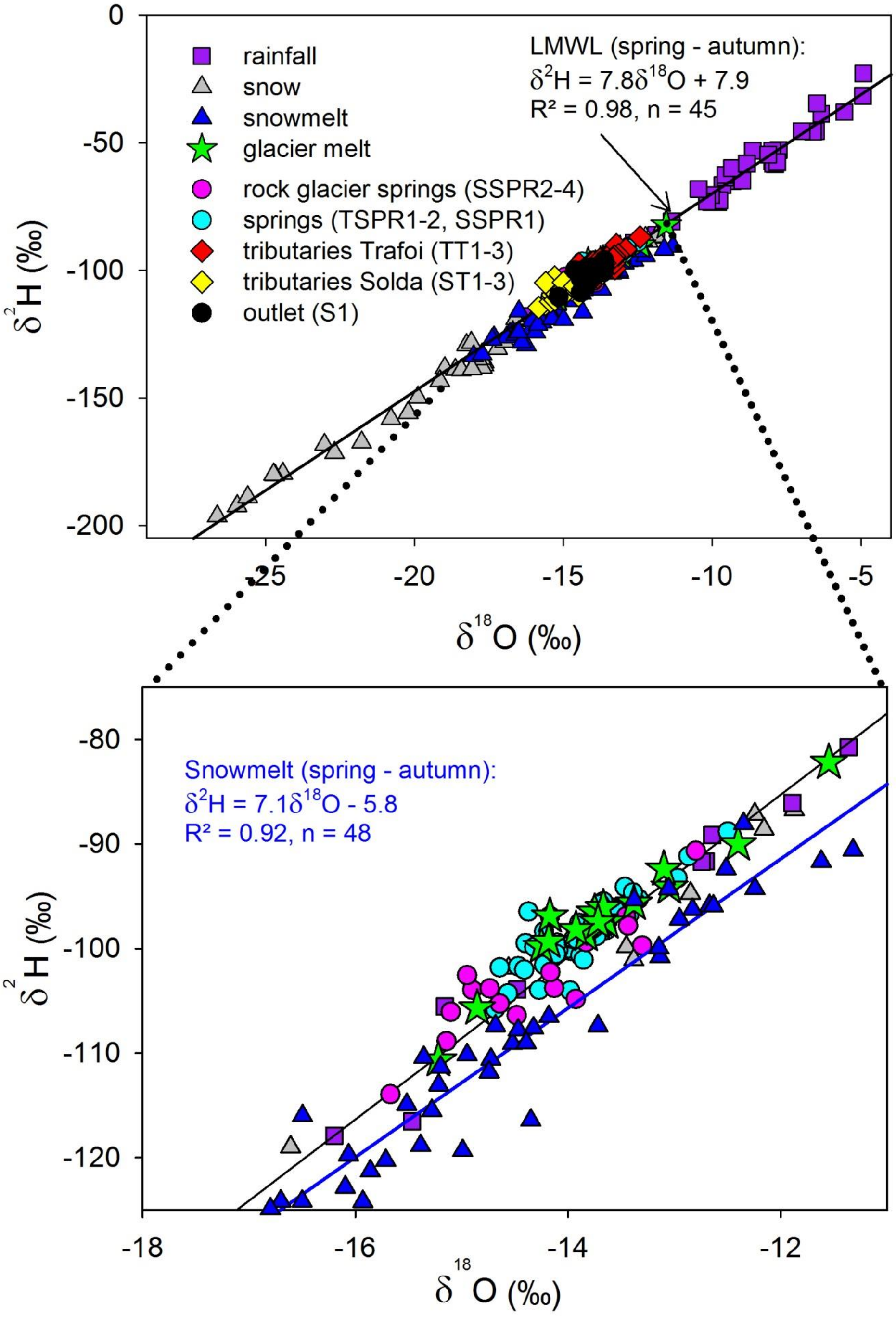

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Figure 2. Meteoric water line of different water sources sampled in the Sulden catchment in 2014 and 2015. The inset shows a zoom on rainfall, snow, snowmelt, glacier melt, and spring waters with the regression line of snowmelt samples collected from spring to autumn.

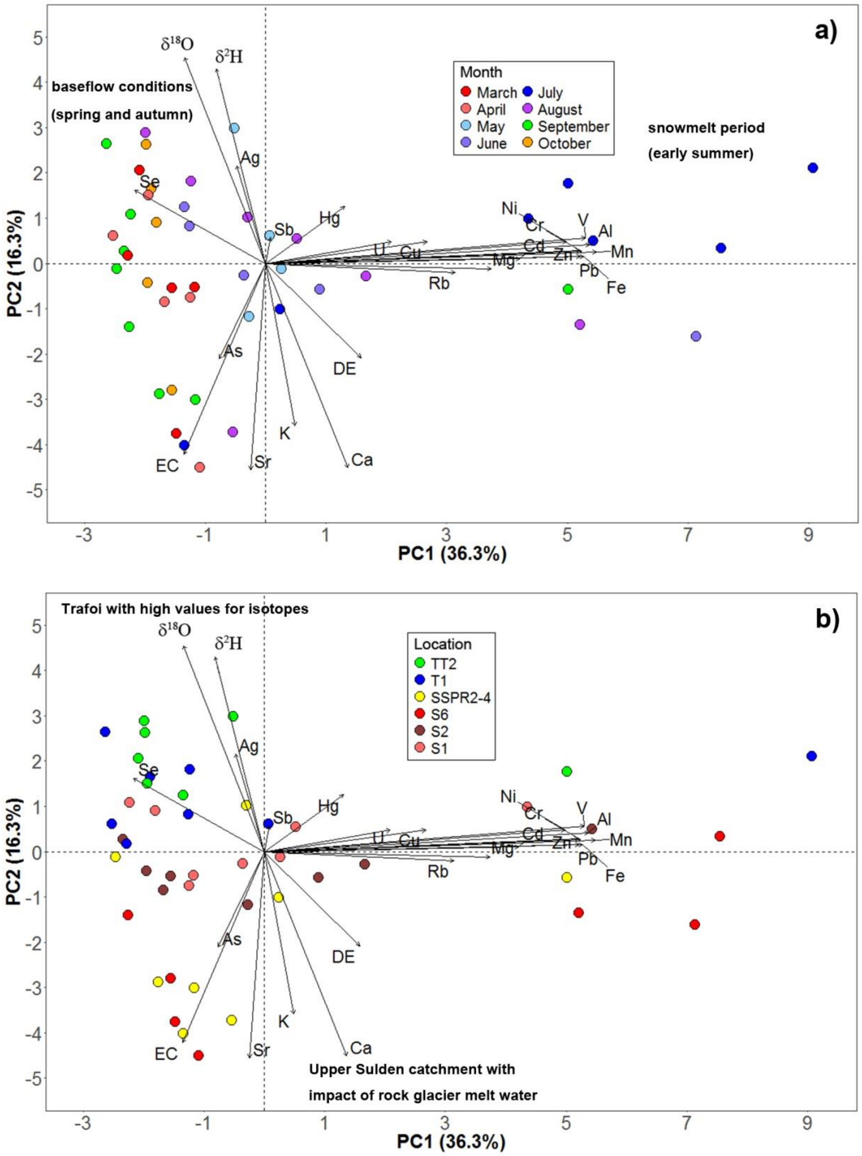

Figure 3. Principle component analysis of element concentrations of stream water and springs draining a rock glacier sampled in the Sulden and Trafoi sub-catchments from March to October 2015. Data based on n = 47 samples are shown in groups according to a) the sampling locations and b) the sampling month.

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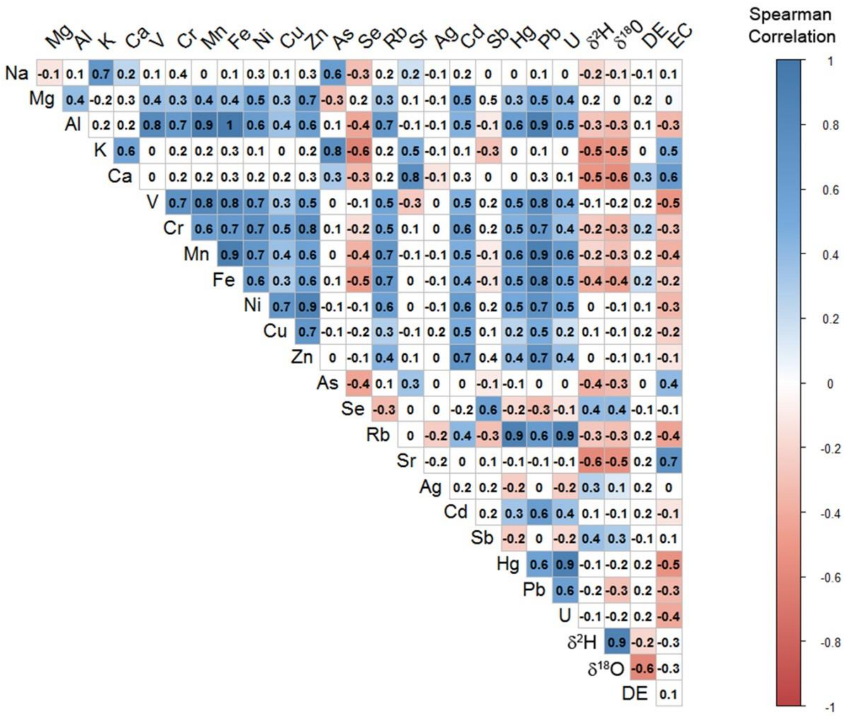

Figure 4. Spearman rank correlation matrix of hydrochemical variables. Values are shown for a level of significance *p* < 0.05.

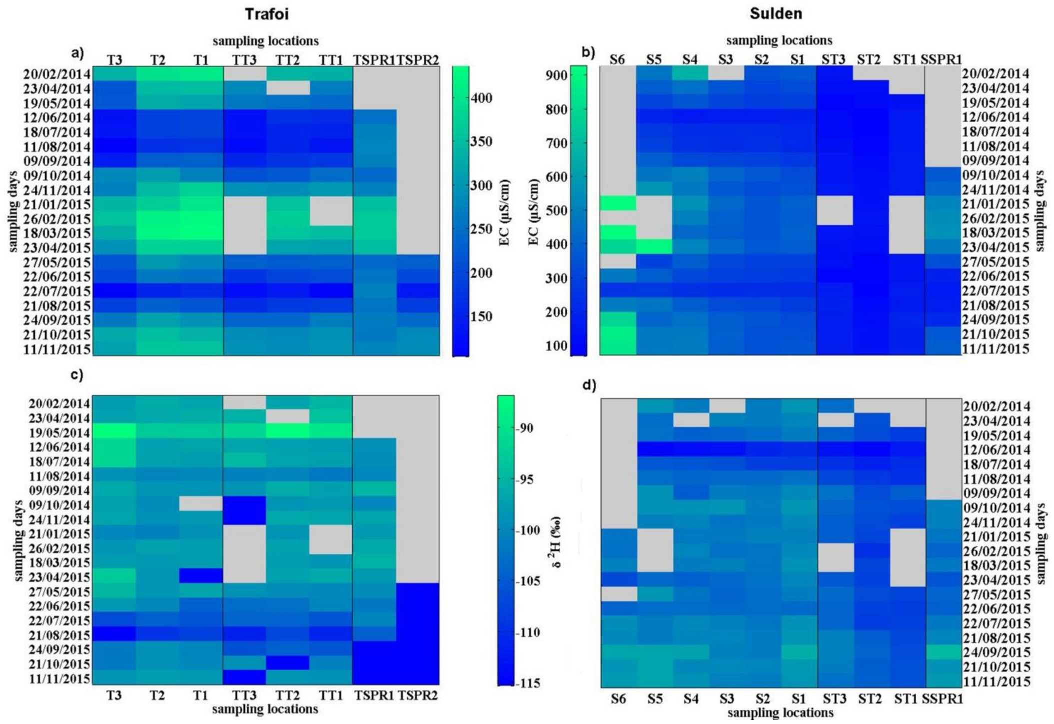

Figure 5. Spatial and temporal variability of EC (µS cm^{-1}) and δ²H (‰) at different stream sections, tributaries and springs within the Trafoi sub-catchment (subplot a and c) and the Sulden sub-catchment (subplot b and d) in 2014 and 2015. The heatmaps are grouped into locations at streams, tributaries, and springs. Grey areas refer to missing sample values due to frozen or dried out streams/tributaries or because the sampling location was included later in the sampling scheme.

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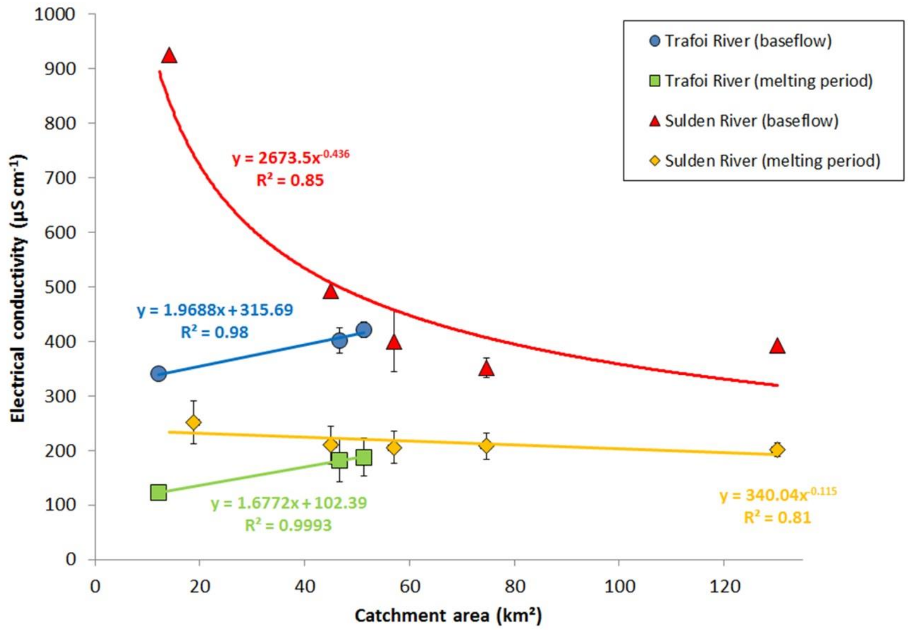

Figure 6. Spatial variability of electrical conductivity along the Trafoi and Sulden River against catchment area. Electrical conductivity is averaged for sampling days during baseflow conditions (21/01/2015, 26/02/2015, and

18/03/2015) and melt period (12/06/2014, 18/07/2014, 11/08/2014, and 09/09/2014).

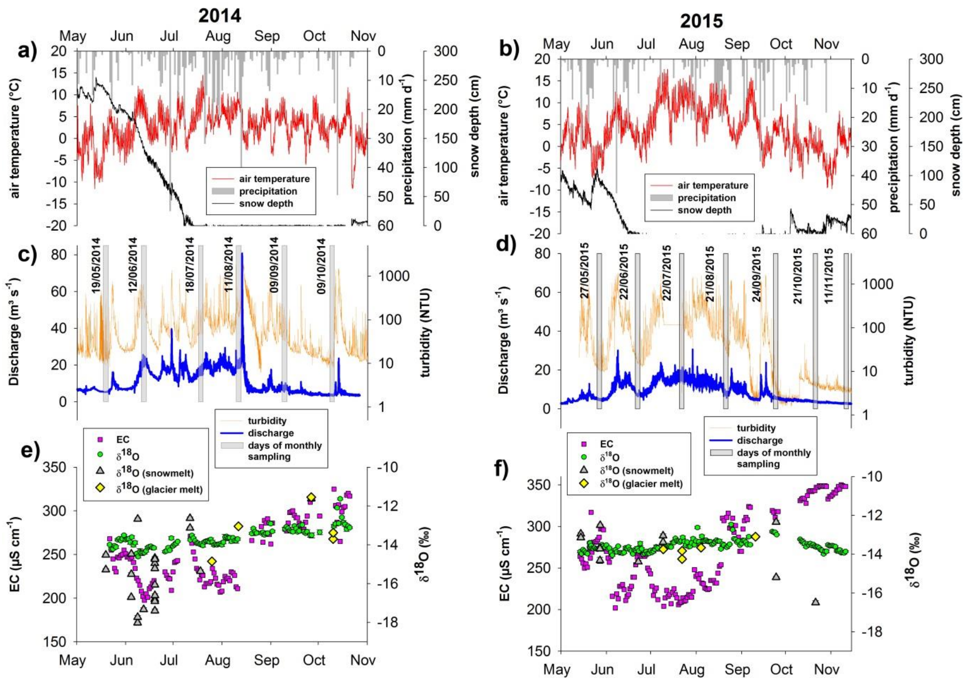

Figure 7. Time series from 2014 and 2015 of a) and b) precipitation, hourly air temperature and snow depth at the AWS Madritsch, c) and d) streamflow and turbidity, e) and f) electrical conductivity and $\delta^{18}O$ of the stream at the outlet station Ponte Stelvio and of snowmelt and glacier melt water. Grey shaded bars indicate the date of monthly sampling carried out in the entire catchment.

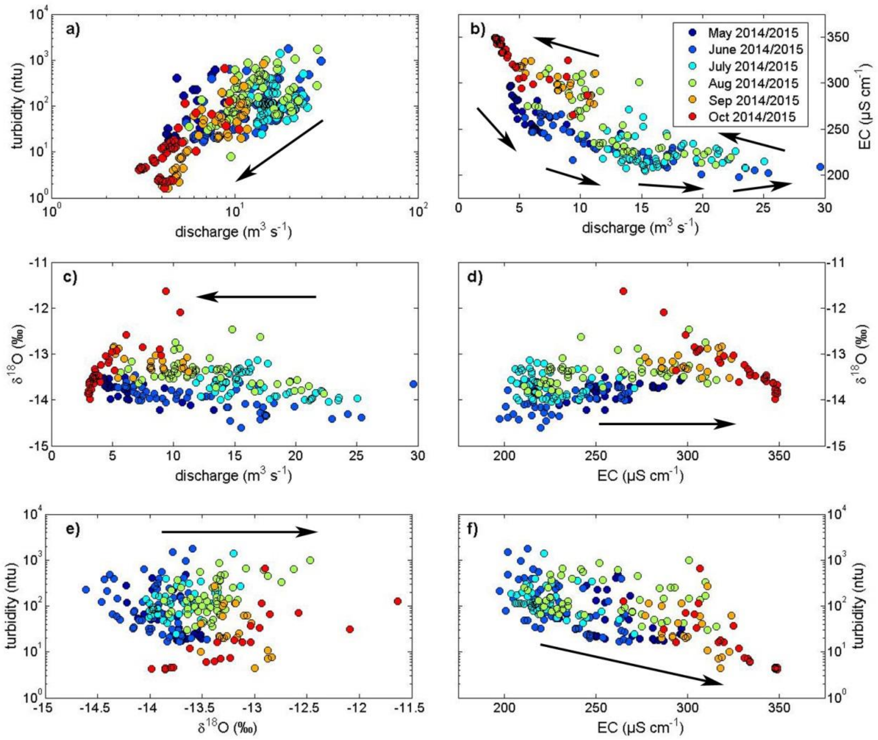

Figure 8. Different combinations of monthly relationships between a) to e) discharge, turbidity and tracers such as EC and δ^{18}O at Ponte Stelvio in 2014 and 2015. The dataset consists of n = 309 samples. Arrows underline the monthly pattern.

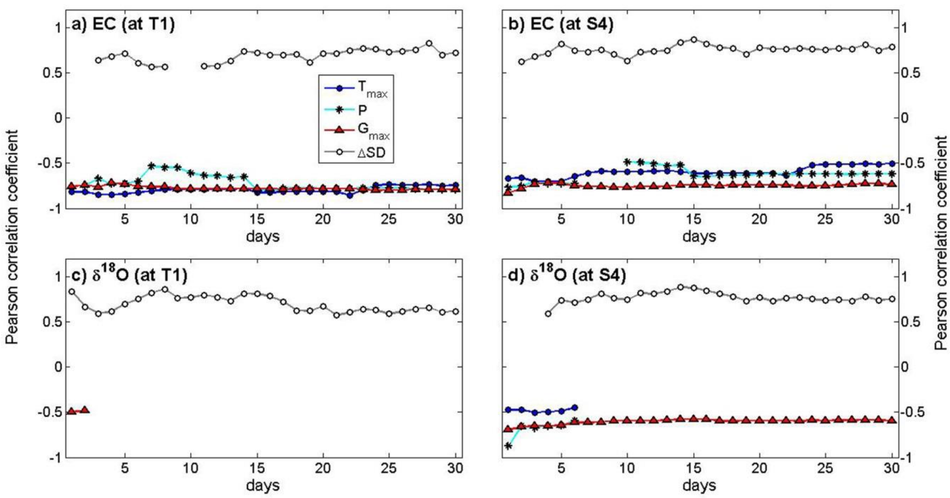

Figure 9. Temporal sensitivity on the agreement of environmental variables and tracer signatures at the selected stream locations T1 (Trafoi sub-catchment) and S4 (Sulden sub-catchment). Values are shown for a level of significance $p < 0.05$ and missing values refer to non-significant correlations.

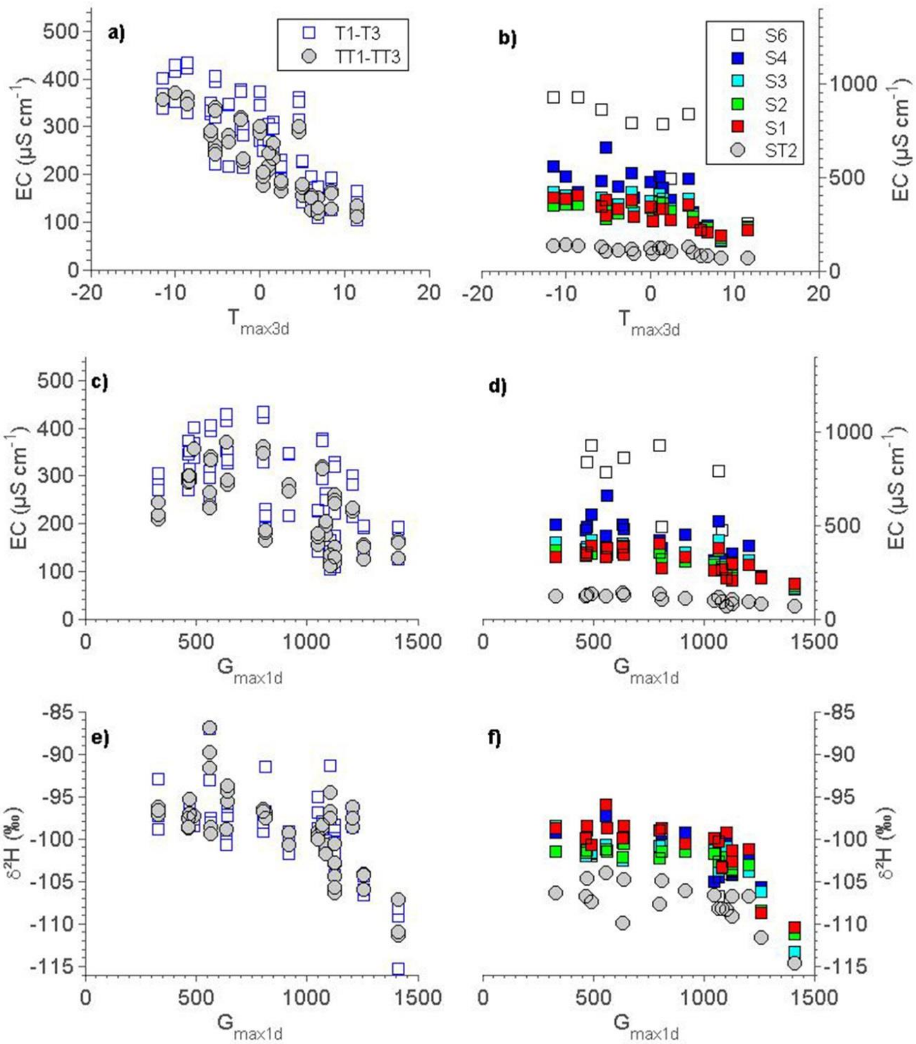

Figure 10. Major controls of environmental variables on tracer signatures in the study area. Subplots a and b show the relationship between electrical conductivity EC and daily maximum air temperature T_{max3d} in the Trafoi and Sulden River respectively. Subplot c and d show the relationship between electrical conductivity EC and daily maximum global solar radiation G_{max1d} in the Trafoi and Sulden River, respectively. Subplot e and f show the relationship between δ^2H and daily maximum global radiation G_{max1d} in the Trafoi and Sulden River, respectively.

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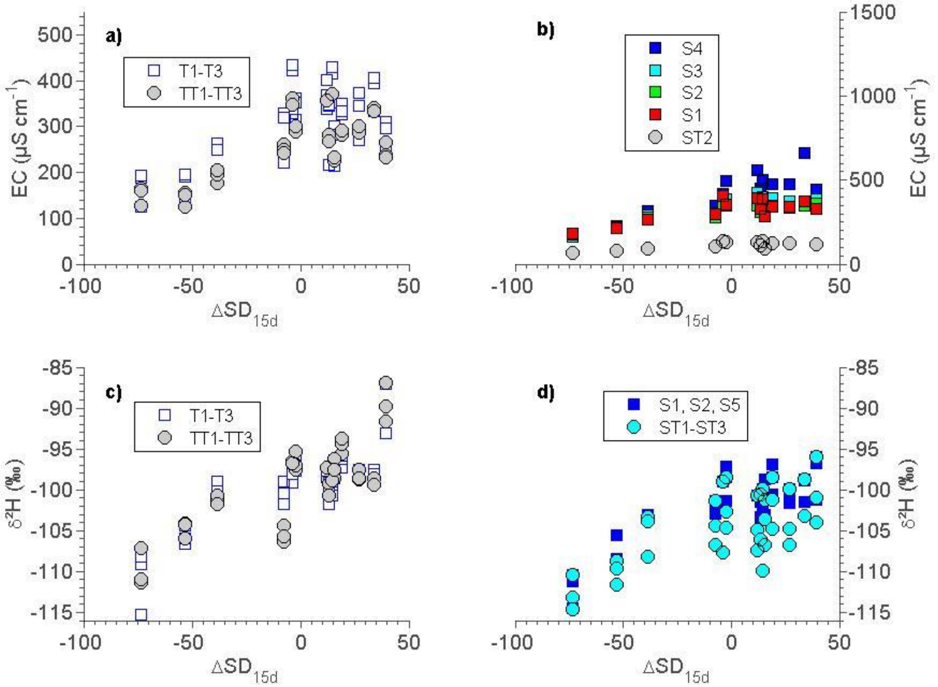

Figure 11. Major controls of environmental variables on tracer characteristics in the study area. Subplot a and b show the relationship between electrical conductivity EC and 15 days snow depth difference ΔSD_{15d} while subplot c and d show the relationship between δ^2H and 15 days snow depth difference ΔSD_{15d} in the Trafoi and Sulden River, respectively.