Contrasting physical and chemical conditions of two springs fed by active rock glaciers

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Abstract

Rock glaciers are increasingly influencing the hydrology and water chemistry of Alpine catchments, with important implications for drinking water quality and ecosystem health under a changing climate. During summers of 2017 - 2019, we monitored the physical and chemical conditions of springs emerging from two active rock glaciers (ZRG and SRG) with distinct geomorphological settings in the Eastern Italian Alps (Solda/Sulden catchment). Both springs had constantly cold waters (1.4 ± 0.1 °C), and their ionic composition was dominated by SO_4^{2-}, HCO_3^-, Ca^{2+} and Mg^{2+}. Concentrations of major ions and trace elements, and values of water isotopes ($\delta^{18}O$, δ^2H), increased towards autumn with an asymptotic trend at SRG, and a positive unimodal pattern at ZRG, where concentrations peaked 60 - 80 days after the end of the snowmelt. Wavelet analysis on electrical conductivity (EC) and water temperature records revealed daily cycles only at SRG, and significant weekly/biweekly fluctuations at both springs attributable to oscillations of meteorological conditions. Several rainfall events triggered a transient (0.5 - 2 hrs) EC drop and water temperature rise (dilution and warming) at SRG, whereas only intense rainfall events occasionally increased EC at ZRG (solute enrichment and thermal buffering), with a long-lasting effect (6 - 48 hrs). Our results, supported by a limited but emerging literature, suggest that: i) the distinctive composition of the bedrock drives different concentrations of major ions and trace elements in rock glacier springs; ii) pond-like and stream-like springs have distinct fluctuations of water parameters at different timescales; iii) peaks of EC/solute concentrations indicate a seasonal window of major permafrost thaw for rock glaciers feeding pond-like springs. These results provide a first quantitative description of the hydrological seasonality in rock glacier outflows, and their hydrochemical response to precipitation events, bringing relevant information for water management in the European Alps under climate change.

1. INTRODUCTION

Climate change is having a profound effect on the availability and quality of Alpine freshwater resources, as the diminishing hydrological contribution from receding glaciers (IPCC, 2019) is paralleled by an increased influence from paraglacial and periglacial landforms (Haeberli, Schaub, & Huggel, 2017; Brighenti et al., 2019a). In particular, active rock glaciers (i.e., creeping bodies of rock fragments providing evidence of mountain permafrost ice) have been addressed as significant water reservoirs at a global scale as their subsurface ice thaws much more slowly than that of glaciers (Jones, Harrison, Anderson & Whalley, 2019). Their hydrological importance (e.g., Brighenti et al., 2019a; Jones et al., 2019) is also promoted by an increasing storage capacity made available by the loss of internal ice (e.g., Wagner, Pauritsch & Winkler, 2016; Jones et al., 2019). Only a small fraction of rock glaciers directly feed surface waters. The seasonal snowmelt is a key hydrological driver of these springs, as their discharge is higher during the snowmelt period and decreases as summer progresses, with short-duration peaks associated with intense rainfall events (e.g., Krainer & Mostler, 2002; Colombo et al., 2018a). During late summer/autumn, only a small fraction of discharge (<5%, e.g., Krainer, Chinellato, Tonidandel & Lang, 2011) can be sustained by internal ice thaw (Colombo et al., 2018b; Brighenti et al., 2019a; Jones et al., 2019). Nonetheless, this small ice melt contribution strongly influences the hydrochemistry of rock glacier springs. Long-term studies on waters fed by rock glaciers attributed the increase of electrical conductivity (EC) and concentrations of major ions and trace elements, which was observed during the last decades, to the progressive thawing of permafrost ice (e.g., Colombo et al., 2018b; Scapozza et al., 2019; Steingruber, Bernasconi & Valenti, 2020).

The seasonal timing of solute export from rock glaciers is particularly important, given the possible effects on drinking water quality (Nickus & Thies, 2015) and freshwater ecology (Brighenti et al., 2019b), with potential effects on entire river networks (Brighenti et al., 2019a). Solute concentrations typically increase from the snowmelt period towards autumn because of the progressive loss of the melting snow component coupled with the increasing contribution from reacted groundwater and permafrost thaw (Williams, Knauf, Caine, Liu, & Verplanck, 2006; Caine, 2010; Krainer et al., 2015; Carturan et al., 2016; Munroe, 2018; Colombo et al., 2018b; Brighenti et al., 2018b). Different studies revealed contrasting patterns of solute increase in rock glacier springs, reporting either an asymptotic behaviour of EC/solute concentrations with the plateau corresponding to autumn-winter (Krainer, Mostler, & Spötl, 2007; Krainer et al., 2015; Nickus & Thies, 2015; Harrington, Mozil, Hayashi & Bentley, 2018), either a positive unimodal trend with peaks during summer (Colombo et al., 2018a). However, the drivers of these contrasting seasonal trends have yet to be investigated. Even the influence of precipitation events on rock glacier hydrochemistry is still being debated. Colombo et al. (2018a) found transient solute-enrichment after intense rainfall events in a rock glacial pond. In contrast, most of studies reported a dilution effect with transient solute-depletion in rock glacier springs (e.g., Krainer & Mostler, 2002; Berger, Krainer, & Mostler, 2004; Krainer et. al., 2007; Harrington et al., 2018).

Rock glaciers have been addressed as efficient thermal buffers, with important implications for freshwater ecology (Brighenti et al., 2020). Springs fed by active rock glaciers are typically very cold (<2°C) because of the coupled influence of the snow and the internal ice, that release latent heat when thawing, and cool down infiltrating rainwater (e.g., Krainer & Mostler, 2002; Krainer et al., 2007; Millar, Westfall, & Delany, 2013; Krainer et al., 2015; Munroe, 2018; Harrington, Hayashi, & Kurylyk, 2017). In fact, rainfall events can either trigger transient drops of water temperature (T_{water}; Geiger, Daniels, Miller, & Nicholas, 2014; Krainer et al., 2015; Winkler et al., 2016; Harrington et al., 2018; Colombo et al., 2018a), or have no thermal effect (Krainer & Mostler, 2002; Krainer et al., 2007) on rock glacier outflows during the snow free period. However, a quantitative analysis aimed at understanding the main parameters driving intensity, duration, and temporal patterns of the response of T_{water} and solute concentrations to precipitation events is still lacking. Rainfall events can also disrupt the diel fluctuations of water parameters in rock glacial springs. These oscillations typically occur during the seasonal snowmelt, and smooth down as summer progresses (Krainer & Mostler, 2002; Berger et al., 2004; Krainer et al., 2007). Periodical fluctuations of EC and T_{water} might also occur over longer timescales (e.g., associated with cold summer periods) but quantitative estimates of such oscillations have been never attempted.

In this study, we describe the physical and hydrochemical patterns of two springs originating from two active rock glaciers in a deglaciating area of the European Alps (Solda/Sulden valley) during the snow free season and investigate similarities and differences in their physical and chemical conditions. We hypothesize that:

- H1) as they both emerge from active rock glaciers, the two springs have comparable physical and hydrochemical attributes, i.e., cold waters, the dominance of calcium, magnesium and sulphates among major ions, and increasing minor and major element concentrations towards autumn as a function of the time elapsed after the snowmelt period.
- H2) evident diel cycles of EC and T_{water} occur during the snowmelt period and the amplitude of these cycles decreases with increasing time elapsed after the snowmelt.
- H3) precipitation events trigger transient responses of EC, whose intensity and duration are controlled by the intensity and duration of precipitation events.

2. STUDY AREA

We studied the permanent springs emerging from two rock glaciers located in two subcatchments (Zay and Solda/Sulden) of the upper Solda/Sulden catchment, Eastern Italian Alps (Figure 1; Table 1). Although the ice abundance and distribution of these rock glaciers is unknown, the two landforms are classified as active according to the rock glacier cadastre of the Autonomous Province of Bolzano/Bozen [APB] (2020a). The geographical, climatic, geological and hydrological settings of the catchment are described in Engel et al. (2019) and Brighenti et al. (2019b). The area belongs to the Austroalpine domain, represented by the crystalline basement and its sedimentary cover (Montrasio et al., 2015). The Zay spring (ZRG) is five meters wide, and it has a very low water velocity (<0.1 m s^{-1}). This ponding spring represents the main outlet of a tongue-shaped rock glacier which is hydrologically connected with the Ausserer Zay glacier (Brighenti et al., 2019b), whose front is located 0.5 km far from the rock glacier rooting zone (APB, 2020a). The geology of the rock glacier subcatchment is dominated by orthogneisses and secondarily quartzphyllites (Montrasio et al., 2015), and a siderite at manganese ore (~1-2 m thick) crosses sub-horizontally its upper cliffs (Mair, pers. comm, 2019). The Sulden spring (SRG) originates ~50 m below a tongue-shaped rock glacier, composed of two merged bodies and partially reshaped by an unsealed road (APB, 2020). SRG runoff is that of a typical high-elevation spring (Brighenti et al., 2019b). The geology of the rock glacier subcatchment is mainly represented by quartzphyllites and michaschists, secondarily by orthogneisses and the sporadic presence of andesites (Montrasio et al., 2015). An automatic weather station (Madriccio/Madritsch, 2825 m a.s.l.) is located within the same glacial cirque as SRG, at 1.4 km distance and 232 m higher elevation. The weather station is located 5.6 km far from ZRG, at 133 m higher elevation. The Rosim sub-catchment separates the weather station area from Zay subcatchment (Figure 1A). A second weather station is located in the Solda/Sulden village (1900 m a.s.l.).

3. MATERIALS AND METHODS

3.1 Field activities and laboratory

The two springs were investigated during three consecutive summers (2017-2019). Data-loggers for T_{water} (HOBO© WaterTempProv2, Onset, Germany; 0.1°C precision) and EC (HOBO© Conductivity Logger ONSET, Germany; 5 µS/cm accuracy), recording at 30 min (2017, 2018) or 15 min (2019) intervals, were deployed at the rock glacier front at the beginning of the snowmelt period (when the sites were accessible), and retrieved in September/October during the flow recession period. EC was not recorded at ZRG during 2017.

Samples were collected monthly during 2017 and 2018, and bi-weekly during 2019 (Figure 1D). At each sampling occasion, we measured T_{water}, EC, and turbidity with portable probes (WTW-Cond-3310 and WTW-Turb-430IR, Germany), and collected water samples for chemical analyses. Samples for the assessment of base chemistry were collected in 500 mL polyethylene bottles, preserved dark at 4°C until delivery to the Hydrochemistry laboratory of the Edmund Mach Foundation (San Michele all'Adige) for the measurement of Alkalinity, pH, EC, HCO_3^-, Ca^{2+}, Mg^{2+}, Cl^-, Na^+, K^+, total nitrogen (TN), NH_4^+-N, NO_3^--N, total phosphorus (TP), PO_4^--P, $SO_4^{2-}$and SiO_2, following standard methods (APHA-AWWA-WPCF, 2017). Additional stream water was filtered through cellulose acetate membranes (0.45 µm pore diameter) into 100 mL polyethylene bottles and acidified in the field (1.5% volume, >65% HNO_3), and delivered to the Ecoresearch S.r.l. laboratory (Bolzano/Bozen) for the measurement of element concentrations (Be, B, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Ag, Cd, Sn, Sb, Ba, Tl, Pb, U, Bi) with Inductively Coupled Plasma Mass Spectrometry (ICP-MS ICAP-Q, Thermo Fischer®). To disentangle the contribution of different water sources to spring discharge, we collected snow, melting snow, glacier ice melt (from Zay and Sulden glaciers during ablation), precipitation (integrated monthly samples of May-October; rainwater containers placed nearby SRG and ZRG and built following IAEA, 2014), and spring water in 50-ml polyethylene bottles. These samples were analysed by a laser spectroscope (Picarro L2130i) at the Free University of Bolzano/Bozen laboratory for the determination of δ^2H (0.1‰ precision) and δ^{18}O (0.25‰ precision).

3.2 Data analysis

Meteorological data for the entire study period were provided by the Hydrographic Office of the APB. The following parameters were considered: snow height (cm, 10 minutes resolution), precipitation (mm, 5 minutes), air temperature (T_{air}, °C; 10 minutes) at the Madriccio/Madritsch station; precipitation (mm) and T_{air} (°C) at the station of the Solda/Sulden village (same time resolution as for Madriccio/Madritsch). This dataset was elaborated to ensure consistent interval records of water parameters (i.e., 30 min intervals during 2017/2018, 15 min intervals during 2019). Based on the Madriccio/Madritsch station, we quantified the meteorological conditions in the area, and estimated for each year the end of the snowmelt period, defined as the date from which the snow cover was absent (< 0 cm) for at least seven consecutive days. Based on this date, we calculated the variable "days after the snowmelt", that we used to describe the seasonal patterns of water parameters while accounting for the contrasting end of the snowmelt period among different years.

Principal Component Analysis (PCA), performed with *factoextra* (Kassambara & Mundt, 2020), *factoMiner* (Husson, Josse, Le & Mazet, 2020) and *corrplot* (Wei et al., 2017) packages in R, was used to visualize the physical and chemical parameters characterizing the two springs and their seasonality. To avoid redundancy, δ^{18}O was discarded a-priori from PCA analysis.

We used a combination of Linear Models (LM), Generalised Linear Models (GLM) and Generalized Additive Models (GAM) to analyse the time series with R studio version 4.0.0 (R Core Team, 2020). To identify trends in the time series of T_{water} and EC, we applied GAMs separately for each station, assuming T_{water} and EC as response variables, days after the snowmelt as smoothing function and year as covariate. To account for autocorrelation of data belonging to the same year, we applied an auto-regressive model of order 1. Moreover, in order to prevent heterogeneity of residuals, we discarded some extremely low and high values in the series before running the GAM analyses, which were performed with *mgcv* package in R (Wood, 2020) by selecting the distribution family based on the Akaike Information Criterion.

The relationship between precipitation events and the variation of water parameters was estimated by determining new variables from the physico-chemical and meteorological dataset. For each precipitation event (minimum intensity ≥5 mm h^{-1} over the recorded interval), we calculated the following parameters: total precipitation (mm), duration (hr), average and maximum intensity (mm hr^{-1}). Two precipitation events were considered separated if their lag time was more than 30 min. The type of precipitation was estimated for each event as a function of the liquid-solid state of water, based on the average air temperature during the event (US Army Corps of Engineers; 1956): rainfall ($T_{air} > 3$°C), rainfall/snow (1°C $\leq T_{air} \leq$ 3°C), snow/rainfall (-1°C $\leq T_{air} <$ 1°C) or snow ($T_{air} <$ -1°C). The transient shifts of EC and T_{water} recorded at ZRG was attributed to precipitation events recorded at the Madriccio/Madritsch station (located in an adjacent subcatchment) because these events were also observed at the Solda/Sulden weather station (located at the Zay closing section), and were therefore catchment scale events.

When a transient shift (δ) above the instrumental precision of T_{water} (> 0.1°C) and/or EC (> 5 μS/cm) was detected, we calculated the following weather variables: lag time (hr) between the onset of the precipitation event and the onset of the response; variation of EC (δEC= EC minimum/maximum – EC at the precipitation onset); variation of T_{water} (δT= T_{water} minimum/ maximum – T_{water} at the precipitation onset); δEC and δT duration (hr; time elapsed to return to pre-event values or to the trend of the corresponding cycles, assessed by visual inspection of EC and T plots). We used LM and GLM to identify the drivers of the physico-chemical response to precipitation events, separately for each station, by setting the absolute variations in the parameters (δEC, δT, δEC duration, δT duration) as response variables and the parameters of precipitation (total precipitation, intensity, maximum intensity, days elapsed after the snowmelt) as predictors, and precipitation type as categorical covariate.

The periodicity in T_{water} and EC time series was analysed by applying the Morlet wavelet transformation with the R *WaveletComp* package v1.1 (Rösch & Schmidbauer, 2018). This spectral analysis investigates periodical phenomena in time series by partitioning the variability in the series into different components according to different frequencies (Morlet, Arens, Fourgeau, & Giard, 1982). We applied separate analyses for each station, year and parameter. With the same package, we also analysed wavelet coherence among T_{water}, EC, and T_{air} to detect consistent fluctuations and phase coherence among these variables.

The statistical differences in the variables between the two monitored springs were tested by the non-parametric Mann-Whitney test (U-statistics) because of the non-normal distribution of their values (retained also after transformation), and/or for inhomogeneous variances. We used the software SPSS (v.25, IBM, 2018) to carry out these statistical analyses.

4. RESULTS

4.1. Climatic conditions during the monitoring period

During the three years of monitoring, the Madriccio/Madritsch station recorded typical alpine conditions, with a mean air temperature of -1.2°C and snow cover lasting for 206-222 days (Figure 1C). An early onset of snow accumulation occurred in 2016 (10th October) when compared with 2017, 2018 (end October) and 2019 (mid-November). 2017 had an earlier end of the snowmelt pulse (10th June) than 2018 (16th June) and 2019 (29th June). Summer 2017 was warmer (August mean air temperature = 8.6°C) and wetter (total precipitation during the snow free period equal to 506 mm) than summers 2019 (7.8°C; 504 mm) and 2018 (7.5°C; 390 mm).

4.2. Hydrochemistry and tracers

Water temperature was very low and constant (1.2 ± 0.1°C) at both springs, where the base chemistry was dominated by SO_4^{2-}, Ca^{2+}, HCO_3^- and Mg^{2+}. At SRG, EC values and SO_4^{2-}, Ca^{2+}, HCO_3^-, Mg^{2+} and K^+ concentrations were significantly higher ($p \leq 0.002$), and turbidity was significantly lower ($p < 0.001$) than at ZRG. Concentrations of the other ions were not significantly different between the two springs. Sr was by far the dominant trace element at both springs, even though Al (up to 146 µg L^{-1}), Fe (328 µg L^{-1}) and Zn (81 µg L^{-1}) at both springs, and Mn at SRG (45 µg L^{-1}) occasionally exhibited high concentrations during early summer (Supplementary S1). Concentrations of As, Sr, and Ba were significantly higher ($p<0.001$), and those of Rb significantly lower ($p<0.001$), at SRG, whereas Al, Mn, Fe, Ni, Cu, Zn, Se, Mo, Pb and U did not significantly differ between the two springs. Ag, Cd, Sn, Sb, Tl, Bi, Cr, V were usually close to their detection limits (1 µg L^{-1}) in both springs.

The first two axes of the PCA explained 72.2% of the total variance (Figure 2A, Table 2). The two stations separated along PC1, with SRG being more solute-enriched, and ZRG having higher concentrations of Rb and higher turbidity. Sample scores spread on a seasonal gradient along PC1 and (only for ZRG) PC2. In fact, both springs exhibited isotopic enrichment, increasing T_{water}, EC, and concentrations of major ions (in particular Ca^{2+}, Mg^{2+}, SO_4^{2-}, and secondary NO_3^- and SiO_2) and trace elements (U and Rb at Zay, and Ba, As and Sr at Sulden) as a function of the days after the snowmelt period, yet with contrasting patterns (Table 2, Figure 4). At SRG, EC and solute concentrations had a linear increase over the time gradient, while ZRG showed a positive unimodal trend with peaks corresponding to 60-80 days after the end of the snowmelt pulse (i.e., early September; Figure 4; Figure 5). In general, solute concentrations were lower in 2018 compared with 2017 and 2019, even if statistical comparisons could not be undertaken (limited number of samples, unbalanced sampling design).

δ^2H and $\delta^{18}O$ were lower at ZRG than at SRG for each sampling occasion (Figure 3), although not significantly different when samples of the same spring were pooled together. Values of δ^2H and $\delta^{18}O$ in stream water samples were significantly lower than in precipitation ($p< 0.001$), and not significantly different from melting snow and glacier ice melt. As summer progressed, the isotopic values of streams progressively enriched, shifting from the signals of melting snow/ice to those of precipitation. The trend of isotopic enrichment as a function of the days after the snowmelt was asymptotic at SRG, and positive unimodal at ZRG (Figure 3). At both stations, SiO_2 significantly increased ($p<0.001$) as a function of the days elapsed after the snowmelt (Figure 4), with a linear trend at SRG (R^2= 0.64) and as a quadratic function at ZRG (R^2= 0.58).

4.3. Trends of water parameters at multiple timescales

The continuous monitoring of EC and T_{water} revealed contrasting patterns for the two springs during the investigated period (Figure 5A). These contrasting patterns were also detected by GAMs (Figure 5B; Table 3), confirming the importance of the days elapsed after the snowmelt pulse as significant explanatory variable. Seasonal minima in water temperature were recorded during the snowmelt period at both stations. As summer progressed, water temperature showed a positive unimodal behaviour at SRG, peaking during mid-summer, and a continuous increase at ZRG. In contrast, EC continuously increased at SRG and had a positive unimodal behaviour at ZRG, where peaks occurred during late-summer before the autumn decline (Figure 5A). Solute concentrations generally followed the same patterns as EC in the two springs (Figure 4).

Wavelet analysis showed distinct cycles in the T_{water} and EC series at the two springs (Figure 6). T_{water} and EC had one-day cycles and one-, eight- to 16-day cycles respectively at SRG. There, the most intense daily fluctuations were detected during the snowmelt period, when both water parameters had late evening minima and mid-day maxima (0.1-0.2°C and 20-70 $\mu S\ cm^{-1}$ fluctuation ranges). The intensity of EC fluctuations at SRG progressively smoothened as summer progressed (e.g., 10-30 $\mu S\ cm^{-1}$ during August), whereas T_{water} had a unimodal trend with larger oscillations (0.2-0.3°C), albeit close to the instrument precision, during August. Daily oscillations parameters occurred earlier in the day as summer progressed (e.g., mid-day maxima and early evening minima), and ceased during September (Figure 6). In contrast, daily fluctuations of water parameters were absent at ZRG, where T_{water} had primary 16-day (0.4°C fluctuations) and secondary 5-day fluctuations (0.1-0.2°C), and these oscillations persisted during the entire summer. For EC, evident cycles were detected at ZRG only starting from mid-August, with six to eight-day primary and 16-day secondary fluctuations (of 10-144 $\mu S\ cm^{-1}$) whose intensity was higher during early September. The bivariate time series of T_{water} and T_{air} revealed coherent fluctuations at different timescales for both springs, almost in phase only at SRG in the beginning of summer (i.e., during the snowmelt). Intense rainfall events, periods of snow cover or cold air conditions recorded at the Madriccio/Madritsch station corresponded to the major interruptions of the diel cycles in T_{water} and EC at the rock glacier springs (Figure 6).

4.4. Effect of precipitation events

The two springs showed contrasting responses to precipitation events. The analysis of the time series at the Madriccio/Madritsch station over the three summers detected 226 precipitation events. At SRG, only one event classified as snow/rainfall (over a total of 18 events), 19 classified as rainfall/snow (over 39) and 40 classified as rainfall (over 148) were associated with a response in EC and/or T_{water}. Almost 94% of rainfall or rainfall/snow events >2 mm occurring when snow cover was absent were associated with a negative response in EC and a positive response of T_{water} (larger than the instrument precision). "Duration of precipitation" was a strong linear predictor of the duration of both $|\delta EC|$ ($R^2=0.65$; $p<0.001$) and $|\delta T|$ ($R^2=0.61$; $F=54.3$, $p<0.001$). "Total precipitation" was the only significant predictor of $|\delta EC|$ (t-value=-8.45, $p<0.001$) in the GLM (Gamma family with Log link, 60.3% deviance explained), as the variables "days after the snowmelt ", and "precipitation intensity" were not significant predictors ($p>0.71$). "Maximum intensity" and "duration of precipitation" were discarded from the model because strongly correlated with precipitation intensity and total precipitation, respectively. When snow cover and snow free periods were analysed separately, “total precipitation” was a weaker predictor of |δEC| during the snow cover periods (t-value=-4.78, $p<0.001$) compared with the latter (t-value=-8.44, $p<0.001$) group. During snow free periods, |δEC| was exponentially related with the predictor total precipitation (R^2=0.67; $p<0.001$). This was also shown by GAMs (Table 2, Figure 5), that detected a stationary and low response of EC (|δEC|= 5.5-11.1 µS cm^{-1}) to precipitation events up to a threshold of around 5 mm, after which |δEC| increased as a function of total precipitation (Figure 7). The interaction between T_{air} and total precipitation (t-value=2.3, p=0.005) was a significant predictor of δT in GLM (Gamma distribution with Log link, 52% deviance explained), whereas only total precipitation was a significant predictor of δT (t-value=4.6, $p<0.001$) when single covariates were considered separately in GLM (Gamma distribution with log link, 48% deviance explained), as T_{air} and maximum intensity of precipitation were not significant covariates (p> 0.24). When only warm periods (T_{air}> 4°C) were considered (Figure 7, black dots), total precipitation was a stronger covariate (t-value=6.3, $p<0.001$) and the deviance explained was considerably higher (67.3%) in the models, where precipitation duration and intensity were discarded because of their strong correlation with total precipitation. The delay between precipitation onset and the associated response in T_{water} and EC ranged between 30 minutes and 2.5 hours, and there was a positive linear relationship between the delay of EC and the delay of T_{water} (R^2=0.77, $p<0.001$).

At ZRG, only seven events influenced T_{water}. The response was weakly negative (-0.2< δT< -0.1°C), long-lasting (1-2 days), and it was recorded only from late July to early September. We found no relationship between the meteorological parameters and δT. Only nine precipitation events (over 96 in total occurred when dataloggers were deployed) influenced EC with values above the instrument precision. These events occurred during snow free and relatively warm periods (T_{air}> 4°C). δEC was positive and exponentially related to total precipitation (R^2=0.79, p=0.001), as also shown by GAMs (Figure 7). The δEC lag-time was in the range of 6-9.5 hours (except 2 hours at one occasion), and we found no relationship between precipitation duration and δEC duration.

5. DISCUSSION

The two springs investigated in this study are typical examples of rock glacier-fed streams, but despite exhibiting many common features display significant differences in hydrochemistry and seasonal trends of water parameters. For this reason, they embody the contrasting hydrochemical patterns that can be found in the sparse literature on the hydrology of active rock glaciers.

5.1. Snow and permafrost drive spring similarities

Our results fully support the first hypothesis (H1) on comparable physical and hydrochemical attributes of active rock glacier outflows. Both springs have very cold waters with only small fluctuations on a daily and seasonal basis, their chemistry is dominated by sulphates, calcium, magnesium and carbonates, and a sharp solute enrichment occurs during late summer under the coupled influence from reacted groundwater and permafrost. This closely agrees with the available literature on the hydrology of active rock glaciers (see Jones et al., 2019). It has long been recognized how snowmelt is a major hydrological driver in alpine settings (Khamis, Brown, Milner, & Hannah, 2015) including rock glacier hydrology (Jones et al., 2019), and we normalised the interannual variability in the snowmelt timing by analysing the seasonal trends of water parameters as a function of the days elapsed after snow cover disappeared. Meteorological variability influences the thermal conditions of rock glaciers, and thus their hydrological behaviour (Colombo et al., 2018a). For example, an anticipated snow accumulation precludes the efficient cooling of the active layer during winter (thermal buffering of snow against cold air), whereas an anticipated snowmelt, and warm summers, accelerate the warming of the active layer and promote ice thawing (Schoeneich et al., 2011). Thus, we attribute the higher EC and concentrations of major ions and trace elements detected at both springs during late summer 2017 to a higher ice-thaw contribution compared with summers 2018 and 2019. This larger contribution was enhanced by an earlier snow cover accumulation (2016), an anticipated snowmelt end, warmer atmospheric conditions, and higher amount of precipitation during summer 2017.

5.2. Lithology and geomorphology drive spring differences

Despite these similarities, the two rock glacier springs differed in several hydrochemical parameters and in their seasonal behaviour. The hydrological connection between the Zay rock glacier and the glacier located upstream (Brighenti et al., 2019b) explains the higher turbidity values (peaking in the seasonal period of glacier ablation), a more depleted isotopic signal, and lower concentrations of major ions recorded at the Zay spring when compared with the Sulden one. The different bedrock composition of the two rock glaciers can explain the distinct concentrations of major ions and trace elements in the two springs. These differences progressively decline towards autumn, when the baseflow contribution becomes the dominant component of rock glacier discharge (Wagner et al., 2019). In fact, rock weathering is considered the major driver of trace element export in rock glacier waters, especially under permafrost thawing conditions (Colombo et al., 2018b), and variations in the availability of weathering products results in the preferential export of different combination of solutes (Steingruber et al., 2020). Rubidium and uranium had higher concentrations at the Zay spring, where the latter element exceeded up to four times the EPA limits for drinking/environmental quality during the window of permafrost thaw. These elements are typical minor constituents of the orthogneisses of the Zay catchment (Mair, pers. comm., 2019). In contrast, concentrations of arsenic, barium and strontium were much higher at the Sulden spring, where the bedrock is enriched in these elements (Engel et al., 2019). Notably, arsenic concentrations exceeded two/four times the limits for drinking/environmental quality but did not show a clear seasonality. This suggests that permafrost thaw does not enhance its concentrations, that might instead be promoted by the common weathering of the calcareous bedrock filling the cracks in this area of tectonic contact. In fact, a recent study attributed the origin of arsenic in rock glacier waters to the presence of As-enriched carbonate ores associated with quartz dykes (Eder, 2019).

The two springs have different fluctuations of water parameters at multiple timescales. This was detected by wavelet analyses, here used for the first time to investigate rock glacier hydrology. Diel cycles of EC and water temperature were only detectable at the Sulden spring, where they were particularly evident during the snowmelt period, and smoothed out as summer progressed. Therefore, the second hypothesis (H2) on the presence of clear diel cycles of water parameters in rock glacier springs must be rejected. The absence of diel cycles at the Zay spring is possibly due to its rock glacier body being very efficient in buffering the snowmelt cycles occurring at its surface, because of the smoothing effect from massive rocky debris. However, wavelet transformations detected fluctuations at weekly to bi-weekly timescales, suggesting that both rock glaciers are hydrochemically and thermally responsive to the medium-term meteorological variability typical of the alpine summer.

5.3. A window of permafrost thaw revealed by water parameters?

The contribution from thawing permafrost in rock glacier outflows is more likely to occur in the late summer, when the 0°C isotherm reaches the interstitial ice triggering partial melting (Williams et al., 2006; Leopold et al., 2011; Colombo et al., 2018a). At Sulden, the increased permafrost thaw contribution might have caused the onset of water temperature decline at the end of August/early September, and of the increase of EC and solute concentrations. The behaviour of water temperature is similar to that previously reported for active (Krainer & Mostler, 2002; Krainer et al., 2007; Krainer, 2015; Munroe, 2018) and inactive (Harrington et al., 2018) rock glaciers, as well as for periglacial taluses (Millar et al., 2013). In contrast, the steady increase of water temperature at Zay suggests a slow thermal response of the rock glacier to the degree-days previously accumulated over the season. At this spring, EC and solute concentrations had a unimodal trend, peaking 60-80 days after the snowmelt end. Similar timing of maximum EC and solute concentrations were detected also by studies on ponds influenced by rock glacier (Colombo et al., 2018a) and permafrost (Colombo et al., 2019), and reveals the major period of permafrost thaw contribution. This "window of permafrost thaw" ends when the cold air and the declining solar radiation typical of autumn promote the re-cooling of the active layer, preventing additional internal ice thawing.

At Sulden, the window of permafrost thaw might be identified differently. In fact, when the isotopic values stabilize in the late summer, any solute enrichment occurring during this period (at least, during dry days) cannot be attributed to the concentration-effect, and might reveal permafrost thaw. Unfortunately, discharge was not monitored in our study, and this hypothesis remains speculative and something to be tested in future research.

5.4. Opposite effects of rainfall events

Several precipitation events which occurred during the monitored period triggered a transient response of EC at the studied springs. The variations were more marked when the snow cover was absent, the precipitation was very likely in the form of rainfall and its amount was sufficiently high. However, our third hypothesis (H3) on the precipitation features driving the response characteristics cannot be accepted. In fact, the intensity and duration of EC response to precipitation events was evident and controlled by the precipitation characteristics only at the Sulden spring, where a rapid (in the order of hours) dilution and warming effect associated to the rainfall events occurred. Although a fast and transient solute dilution from liquid precipitation was already reported in rock glacier outflows (Krainer & Mostler, 2002;

Krainer et al., 2007; Harrington et al., 2018), our study is the first to provide a measure of intensity and duration of these responses, suggesting a threshold of 5 mm rainfall after which the increase of precipitation strongly correlates with an increased effect on EC and water temperature. The positive thermal response to rainfall (during snow free periods) at Sulden, which is unique in the literature (Krainer & Mostler, 2002; Krainer et al., 2007; Geiger et al., 2014; Krainer et al., 2015; Winkler et al., 2016; Harrington et al., 2018; Colombo et al., 2018a), might be promoted by the increased subsurface water flow coming from the surrounding moraine deposits, which mixes with the rock glacier waters before outflowing at the spring. In fact, the Sulden spring emerges 50 m from the rock glacier terminus.

At the Zay spring, a long-lasting effect of rainfall events was observed in terms of solute enrichment, with an intensity correlated to the precipitation amount, yet only for the events where we could observe an effect. In fact, only a few rainfall events triggered a response of EC, and we could not identify the event parameters responsible for this response. A similar hydrochemical response to rainfall events was described in a rock glacier pond by Colombo et al. (2018a), who concluded that rainfall events occurring during the snow free season enhance solute concentrations because infiltrating rainfall flushes out the weathering products derived from permafrost thaw.

5.5. Potential drivers of contrasting hydrological patterns in rock glacier outflows

Growing evidence suggests the importance of a fine-grained basal layer with low hydraulic conductivity, which constitutes a groundwater storage system in rock glaciers. This sub-permafrost layer is the major control of base flow conditions, with fractures and depressions occurring in the basal bedrock playing a minor contributory role (Jones et al., 2019; Wagner, Brodacz, Krainer & Winkler, 2020). Most of the rainwater is quickly exported from rock glaciers across lateral flows in the supra-permafrost layer, which is made of coarse blocky materials with high hydraulic conductivity. The presence of fractures and ice-free areas in the ice-sediment matrix allows some water to cross the intra-permafrost zone, enhancing the recharge of the sub-permafrost aquifer (Wagner et al., 2020). With this model in mind, and building on previous studies, we hypothesize that different hydromorphological settings in rock glaciers promote distinct hydrochemical behaviour at different timescales. Hence, we suggest that two major types of rock glacier-fed springs exist, namely the stream-like and the pond-like systems (Figure 8).

Stream-like springs such as the one at Sulden emerge and flow in defined channels, they have an asymptotic behaviour of solute concentrations as summer progresses, and they respond to snowmelt cycles and rainfall events with a direct solute dilution (Figure 8A). The Sulden rock glacier lays on steep slopes, and this might promote a quick water routing across a steep sub-permafrost aquifer. An efficient mixing of this groundwater base flow with the rainfall/snowmelt water (which has previously crossed the unsaturated layer across lateral flow) would results in the solute dilution that we observed at the spring after rainfall events and snowmelt cycles. Intra-permafrost flow may become active during autumn, when the active layer is at its minimum. In this period, most of the infiltrating water can be routed at greater depths and recharge the sub-permafrost aquifer, instead of being quickly exported across the supra-permafrost flow, and leading to lacking response of EC to rainfall events. In this period, the weathering products resulting from permafrost thaw would be released into the bulk sub-permafrost flow, and exported as base flow from the rock glacier.

In contrast, pond-like springs such as the one at Zay emerge as ponded systems, they have a unimodal behaviour of solute concentrations as summer progresses, and only a buffered effect of solute enrichment from rainfall events occur, without any daily influence from snowmelt cycles (Figure 8B). The Zay rock glacier has a gentle slope for most of its longitudinal profile, the water velocity at the spring is very low, and a wet meadow located at the rock glacier forefields indicates a sparse water table emergence (Hayashi, 2020). A prevalence of slow and distributed water pathways in the rock glacier interior might cause the buffered hydrological behaviour of these rock glaciers (Winkler et al., 2016; Harrington et al., 2018). The ponding process reveals the emergence of the aquifer close to the rock glacier front upstream. Displacement (translatory flow; see Sprenger et al., 2019) and/or uplifting mechanisms (e.g., transmissivity feedback; Bishop, Seibert, Köhler & Laudon, 2004) have been suggested as key processes promoting the outflowing of the old groundwater during rainfall events in aquifers, and have been also suggested to occur in periglacial taluses (Muir, Hayashi & McClymont; 2011). These hydrological processes would explain the solute enrichment occurring after rainfall events at the Zay spring, in particular during the window of permafrost thaw when the rock glacier aquifer is enriched in solutes flushed from the intra-permafrost layer.

Unfortunately, these hypotheses relating to contrasting geomorphological settings are based on a low number of studies, and the hydrological regime and internal structure of the Zay and Sulden rock glaciers are still unknown. Further research involving hydrological, hydrochemical and geophysical characterisation of rock glaciers is needed to better elucidate the linkages between the internal structure of these landforms and their hydrochemical behaviour at multiple timescales, and verify the existence of these two major systems with distinct hydrological behaviour.

6. CONCLUSIONS

This study presents a detailed description of the seasonal trends in water temperature and solute concentrations of rock glacier springs. It is the first quantitative description of the fluctuation of these hydrochemical parameters at multiple timescales, and of their response to precipitation events. Our results provide additional insights on the importance of hydromorphological settings in driving the physical and chemical attributes of active rock glacier outflows. The seasonality of these springs is dictated by the fading role of the snow paralleled by an increasing influence from internal ice, resulting in continuously cold waters and increasing concentrations of major ions and trace elements as summer progresses. Based on a limited literature, we hypothesize that the distinct patterns of water routing determine the hydrochemical behaviour of rock glacier springs. Stream-like springs with channelised base flow pathways have diel cycles, respond quickly and frequently to rainfall events and are characterised by a solute dilution response caused by the efficient water routing. Pond-like springs relying on a shallow and distributed water table, have smoothed diel cycles of water parameters, and react slowly to changing atmospheric conditions and, in particular, to rainfall. These events can trigger a solute enrichment, likely promoted by displacement or uplifting mechanisms occurring in the rock glacier aquifer. A seasonal window of major permafrost thaw can be detectable for these rock glacier springs because of the efficient export of weathering products during this period. Given the increasing hydrological influence of rock glaciers in deglaciating catchments, a better understanding of the drivers for distinct physical and hydrochemical patterns has important implications for water management under climate change.

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Data Availability statement

The data supporting our findings are available upon reasonable request to the corresponding author.

Conflict of Interest Statement

The authors declare no conflict of interest.

Figure 1. Main features of the study sites. A) Geographical location of the Zay and Sulden subcatchments in the European Alps; the two areas are separated by the Rosim subcatchment (not highlighted in the figure); B) Location in a DEM map of the Zay spring and C) Sulden spring. D) Weather conditions at the Madriccio/Madritsch station (APB, 2020). Monthly values for: total precipitation (Prec., in mm, black columns), average snow cover thickness (snow, in cm, grey area) and average air temperature (T_{air}, °C, black line) during different years (that are separated by dotted vertical lines). The snow free seasons, when only transient snow events occurred, are highlighted in green bars. The accumulation of winter snow started the 10th October in 2016. Vertical black arrows indicate the major sampling dates (SAMPLING).

Figure 2. A) PCA biplot. Ellipses group the samples of the two springs (continuous line= ZRG, dashed line= SRG). B) Correlation matrix of the selected variables, with blank cells corresponding to correlations not significant ($p>0.01$).

Figure 3. Scatterplot of isotopic values (δ^2H) as a function of the days after the snowmelt variable. Note: points of precipitation refer to water of multiple events collected on a bi-weekly/monthly basis, and collected the day of reference. Interpolation lines represent LOESS smoothing curves.

Figure 4. Seasonal trends of water parameters over summer, as a function of the number of days after the snowmelt (reference Madriccio/Madritsch station, APB; 2020) at SRG (left panels) and ZRG (right panels). In each scatterplot, distinct parameters are shown in different colours and shapes, and their scale corresponds to that of the axis where the name of each parameter is placed. Interpolation lines represent LOESS smoothing curves.

Figure 5. A) Series of EC and T_{water} (daily average) at the two springs over the logging period. As a reference, we provide the daily values of air temperature and total precipitation, and the presence of snow cover at the Madriccio/Madritsch station (Source: APB, 2020). B) Model fit of GAMs analyses performed with T_{water} and EC in the two springs, setting the days after the snowmelt as a smoothing term (see Table 3 for model numerical results).

Figure 6. Wavelet power spectrum of electrical conductivity and water temperature recorded at SRG and ZRG during each summer. As a reference, the daily values of air temperature (°C, black line), snow height (cm, grey area) and total precipitation (mm, grey bars) at the Madriccio/Madritsch station are plotted in the centre of the figure (Source: APB, 2020). Horizontal axes represent the timeline, shown only in the plot of weather conditions. Vertical axes indicate the fluctuation period (days). The wavelet power spectrum (coloured space, 250 power levels) represents the affinity of each variable to each period over the series. White contours delimitate the areas of significant periods ($p<0.01$, method "white noise"), and the black line indicate a ridge in the power spectrum (i.e., strongest affinity of the variable with the corresponding period).

Figure 7. Scatterplots of precipitation events and the associated response of water parameters at the two springs. Confidence intervals of linear (LM) and Generalised Additive (GAM) models are fitted. Red points indicate the values that were discarded from the models because snow cover was present (Event - δEC plot) or because T_{air} was low (< 4°C; event - δT plot) when precipitation was occurring.

Figure 8. Schematic representation of the distinct behaviour of rock glacier springs at multiple timescales during the snow free season. A) Stream-like springs such as the Sulden one exhibit A1) an asymptotic behaviour of solute concentrations as summer progresses. A2) Rainfall events (arrows, thickness and length indicate increasing precipitation amount) cause a rapid dilution effect at these springs, where A3) diel fluctuations of solute concentrations are evident soon after the snowmelt period, and progressively smoothen towards the end of the summer. B) Pond-like springs such as the Zay one exhibit B1) a unimodal behaviour of solute concentrations as summer progresses, with peaks corresponding to the window of permafrost thaw (WPT). B2) Rainfall events can cause a delayed and long-lasting effect of solute enrichment at these springs, where B3) diel fluctuations of solute concentrations do not occur. Callouts indicate the number of studies supporting this evidence (see main text for references).