ORIGINAL ARTICLE

Climate Change-Induced Changes in the Chemistry of a High-Altitude Mountain Lake in the Central Alps

Sandra M. Steingruber[1] · Stefano M. Bernasconi[2] · Giorgio Valenti[3]

Abstract

Mountains are among the most sensitive ecosystems to climate change, and one of the most evident signs of climate-related effect is the continuous net loss of ice from the cryosphere. Several studies showed that meltwater from glaciated and perennially frozen areas can profoundly affect alpine aquatic ecosystems. Here, we present the impressive temporal increase in solutes in Lake Leit, a mountain lake in the Central Alps that is impacted by an active rock glacier. During the last 30 years, concentrations of sulfate and base cations increased by factors of 4 and 3, respectively. Atmospheric deposition, the only catchment external source, could be excluded as possible cause. The inlets have sulfate and base cations concentrations that were up to double the concentrations of the lake outlet confirming the presence of catchment internal sources. The highest concentrations were measured in the springs at the bottom of the rock glacier. Ground surface temperatures of the rock glacier indicated a high probability of permafrost occurrence, while the annual mean air temperature after the mid-1980s showed continuously positive deviations from the long-term average values (period 1961–1990) with increasing values after 2010. δ^{34}S of sulfate in the inlets and the outflow indicated that sulfate in Lake Leit mainly derived from dissolution of gypsum/anhydrite even if its presence is not confirmed by the Geologic Atlas of Switzerland. Because of these results, we postulate the presence of subsurface traces of sulfate-bearing evaporites, probably associated with Triassic metasediments. These deposits are very common in the closer surroundings. We further hypothesize that the thawing of permafrost affects the flow path of water enabling its contact with fresh highly weatherable minerals increasing the overall weathering rate and shifting the relative ionic composition in the discharge toward the ions that originate from the most soluble minerals. This study shows that increased permafrost thawing in the future can influence water quality in high-alpine settings.

Keywords Climate change · Mountain lake · Alps · Permafrost · Rock glacier · Water chemistry

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1 Introduction

Human activities are dramatically impacting the world's climate (IPCC 2018). Particularly, mountains are among the most sensitive ecosystems to climate change (Pepin et al. 2015). One of the most evident signs is the continuous net loss of ice from the cryosphere (IPCC 2013). Meltwater from glaciated and perennially frozen areas can profoundly affect alpine aquatic ecosystems (Brighenti et al. 2019; Colombo et al. 2018; Jones et al. 2019; Slemmons et al. 2013). Particularly, water bodies and streams located downstream of rock glaciers often show increased electrical conductivity with calcium, magnesium and sulfate being the most important contributors, especially at baseflow conditions (Baron et al. 2009; Ilyashuk et al. 2018; Lecompte et al. 2008; Rogora et al. 2020; Scapozza et al. 2020; Thies et al. 2007, 2013; Williams et al. 2006). In addition, permafrost-fed freshwater bodies and streams can be enriched in metals such as aluminum, barium, copper, cobalt, manganese, nickel, strontium, zinc partly exceeding the maximum permissible levels of drinking water (Ilyashuk et al. 2014; Nickus et al. 2015; Thies et al. 2007, 2013). Several studies observed that rock glaciers are more common on metamorphic bedrock (Chueca 1992; Johnson et al. 2007; Kellerer-Pirklbauer 2007; Seppi et al. 2012) and increased concentrations of sulfate in surface waters situated on crystalline bedrocks and influenced by cryogenic features have often been ascribed to oxidation of sulfides (Ilyashuk et al. 2018; Lecompte et al. 2008; Mast et al. 2011; Salerno et al. 2016; Williams et al. 2006), in particular pyrite, a common mineral in many sedimentary, metamorphic and igneous rocks (Tranter and Raiswell 1991). Here, we present and discuss the causes of the large temporal increase in solutes in a mountain lake in the Central Alps impacted by an active rock glacier and enquire about the possible reasons for this trend.

2 Study Area and Methods

2.1 Study Area

Lake Leit (Long 8°43′17″, Lat 46°27′55″) is a high-mountain Swiss lake situated in the Lepontine area of the Central Alps in the Canton of Ticino at an altitude of 2260 m a.s.l. (Fig. 1). It has a surface area of 3.2 ha and a maximum depth of about 13 m. Its catchment is 0.524 km² and has average and maximum altitudes of 2403 m and 2713 m a.s.l. (Pizzo Campolungo), respectively, and an average slope of 50%. There are a surface outflow (Out, Fig. 2a) and one main persistent surface inflow creating a small delta (I5, Fig. 2a), both represented in the National Map 1:25,000 (Federal Office of Topography (Swisstopo) 2012). A smaller persistent surface inflow creates a second delta (I4, Fig. 2a). Springs close to the lake border have been observed at site I1 and at the bottom of the rock glacier (I2, I3, Fig. 2a).

The catchment is mainly covered by debris and sand (44%) and rocks (32%), while vegetation is confined to small areas (11% stony alpine pasture and 7% unproductive herbaceous vegetation) (Federal Statistical Office 2017).

The tectonic of the Lepontine Alps is characterized by the presence of a pre-Triassic basement and, at several localities, a metamorphosed sedimentary cover of late Paleozoic and Early Mesozoic age (Gieré et al. 2011). The catchment of Lake Leit is situated on the Simano nappe that consists mainly of uniform and rather homogenous metagranitoids
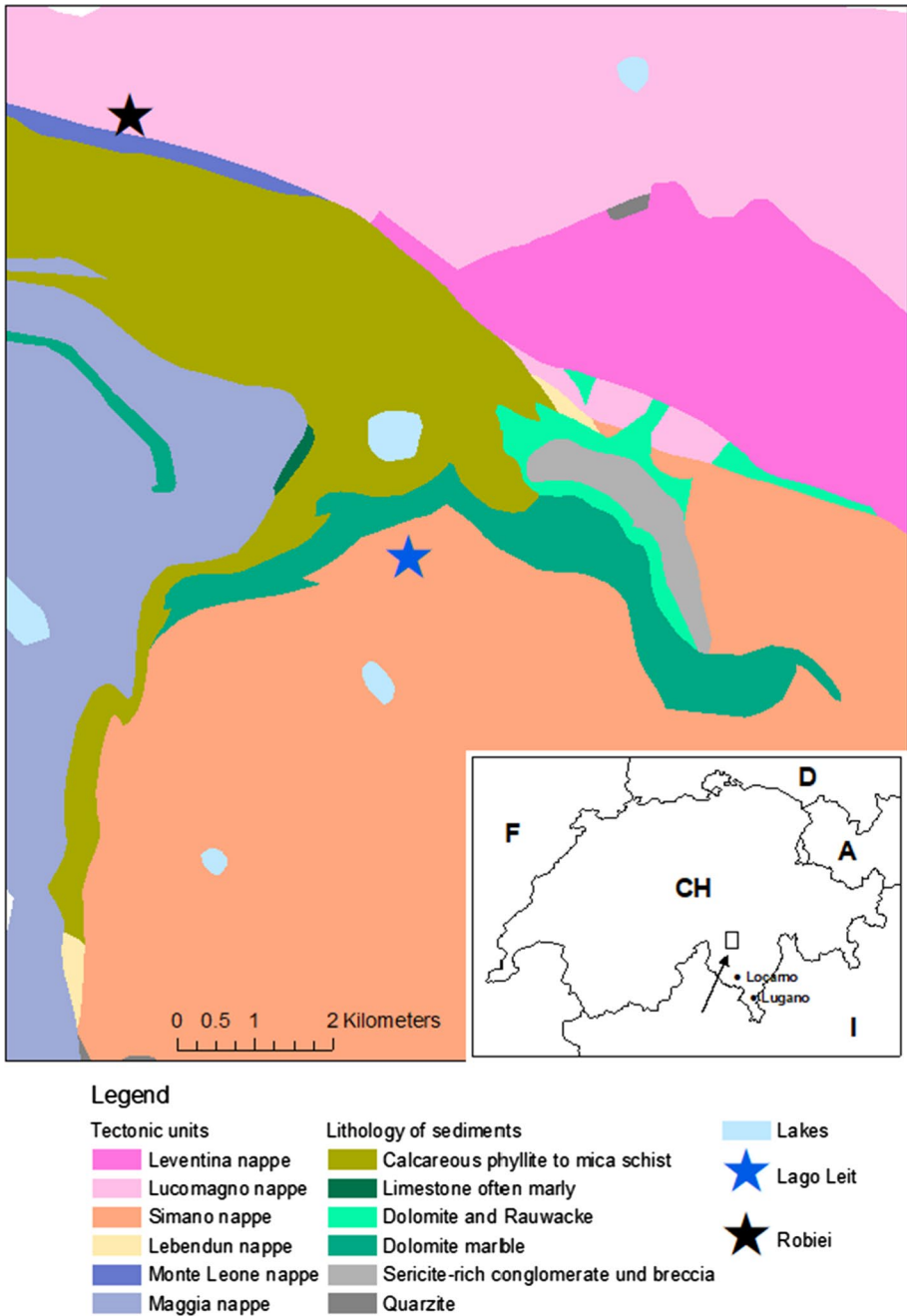
Fig. 1 Tectonic units and lithology of the sediments around the study site extracted from the tectonic map of Switzerland 1:500,000 and the Geologic map of Switzerland 1:500,000 (Swisstopo 2011)
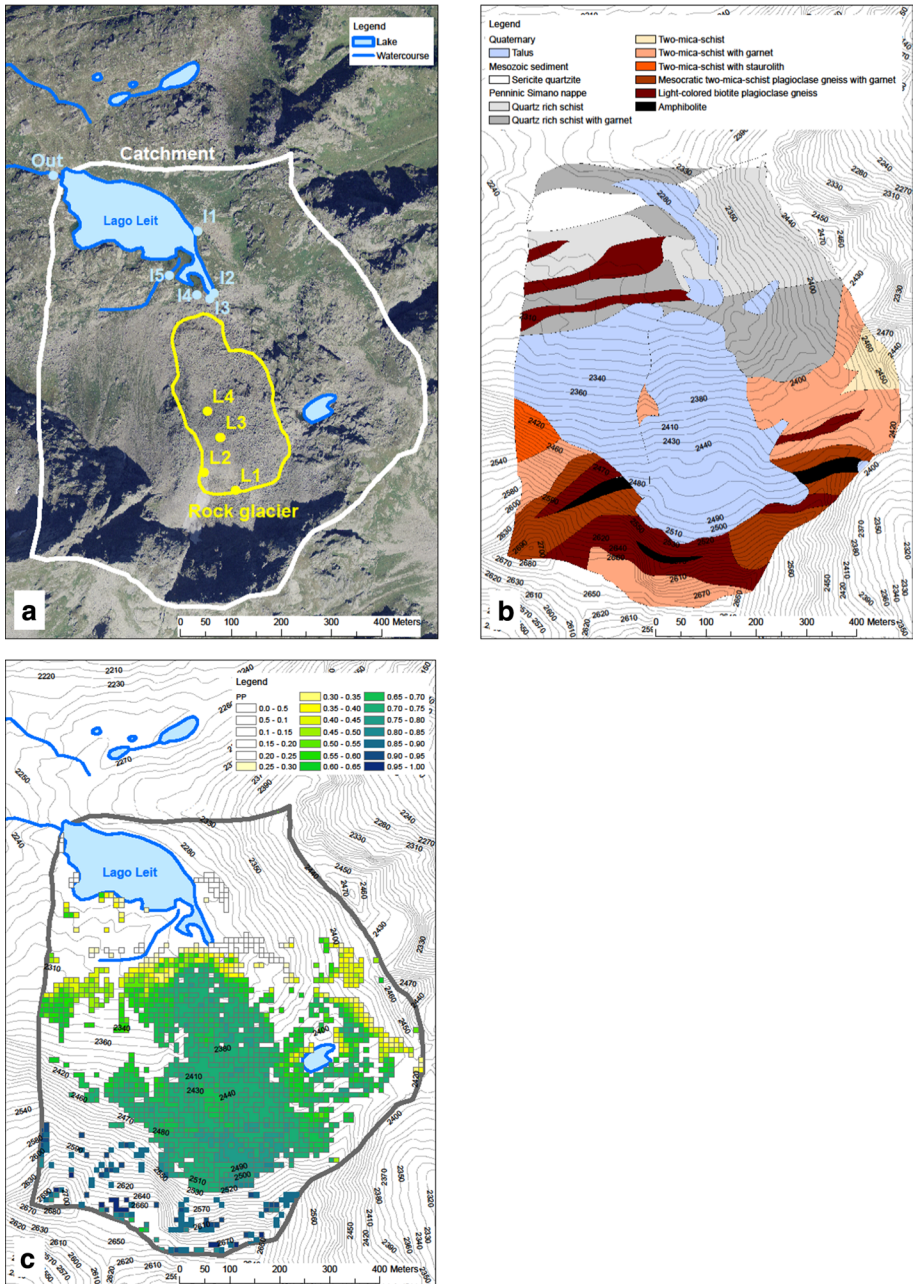
Fig. 2 Catchment of Lake Leit. **a** Sampling sites of the lake outlet and inlets (Out, I1, I2, I3, I4, I5) and of the ground surface temperature of the rock glacier (L1, L2, L3, L4), **b** geology extracted from the Geologic Atlas of Switzerland 1:25,000 (Swisstopo 2015), **c** probability of permafrost occurrence PP (Deluigi et al. 2017)

(Berger et al. 2005), very close to the triassic metasediments of the Campolungo region that is dominated by dolomitic marble (Bianconi 1971) (Fig. 1). The geology of the catchment itself is shown in Fig. 2b. The lithology is dominated by gneiss, quartz rich schist, mica-schist and plagioclase gneiss. A narrow area of Triassic rocks consisting mainly of quartzite passes under the lake. The catchment is also characterized by the presence of an active rock glacier covering 10% of the area (5.5 ha, Deluigi et al. 2017).

2.2 Meteorological, Hydrological, Climatic and Cryospheric Characteristics

Average annual precipitation at the study site was estimated to be 1834 mm between 1983 and 2017. The value corresponds to the mean of the values extracted from 5-year mean precipitation maps provided by the company Meteotest and then improved by the author (for details, see Steingruber 2018). Evaporation was estimated to be around 22% and was calculated dividing the evaporation volume extracted from the Swiss evaporation map of the period 1971–1990 (Menzel et al. 1999) with the precipitation volume extracted from the precipitation map of the period 1971–1990 for the European Alps (Schwarb et al. 2001). A mean areal hydraulic load calculated as the ratio between the water discharge and the lake area of 23 m yr^{-1} can be derived. The mean depth of the lake is not well known; however, assuming a perfectly cone-shaped bathymetry, a residence time of about 2 months can be estimated.

During the last three decades, air temperature in the Canton of Ticino increased between 0.3 and 0.5 °C per decade and in the previous 150 years between 0.09 and 0.11 °C per decade (MeteoSwiss 2012). The temperature deviation from the average (11.6 °C) of the normal period (1961–1990) at the MeteoSwiss weather station at Lugano (273 m a.s.l., Fig. 1), with the longest temperature records in the area, was positive and continuously increased after the mid-1980s (Fig. 3a). The temperature deviation from the average of the monitoring period (1992–2018) at the MeteoSwiss weather station at Robiei (1890 m a.s.l., Fig. 1), the most representative station close to the study site, shows that temperature further increased after 2010 (Fig. 3b).

The permafrost probability (PP) map of Deluigi et al. (2017) shows that the presence of permafrost is very probable under the rock glacier (Fig. 2c). In order to confirm its presence, four UTL-3 Scientific Dataloggers (Geotest AG, with an accuracy of ± 0.1 °C) were positioned in autumn 2015 at four locations on the rock glacier to measure ground surface temperature (GST) (see L1, L2, L3, L4 in Fig. 2a). GST is defined as the surface or near-surface temperature of the ground (bedrock or superficial deposit), measured in the uppermost centimeters of the ground (http://www.permanet-alpinespace.eu). Every summer the dataloggers were collected for data recovery and necessary revisions and repositioned in autumn. Unfortunately, during winter 2016/2017, all four dataloggers did not work, during winter 2017/2018 there were problems with logger L1 and L3 and during winter 2018/2019 with logger L3. To determine the possible presence of permafrost, from the GST data, we extracted the winter equilibrium temperature (WEqT). The WEqT corresponds to the GST that has progressively stabilized and reached equilibrium below the snow cover of a certain depth. According to Hoelzle (1992), the presence of permafrost is probable at WEqT < − 3 °C, possible at WEqT from − 3 to − 2 and unlikely at WEqT > − 2 °C. To estimate the daily snow cover, data measured at Robiei by the Swiss Federal Institute for Forest, Snow and Landscape Research (WSL) were analyzed, while daily mean temperature measured at Robiei by MeteoSwiss was used as an indicator for seasonal temperature variations.
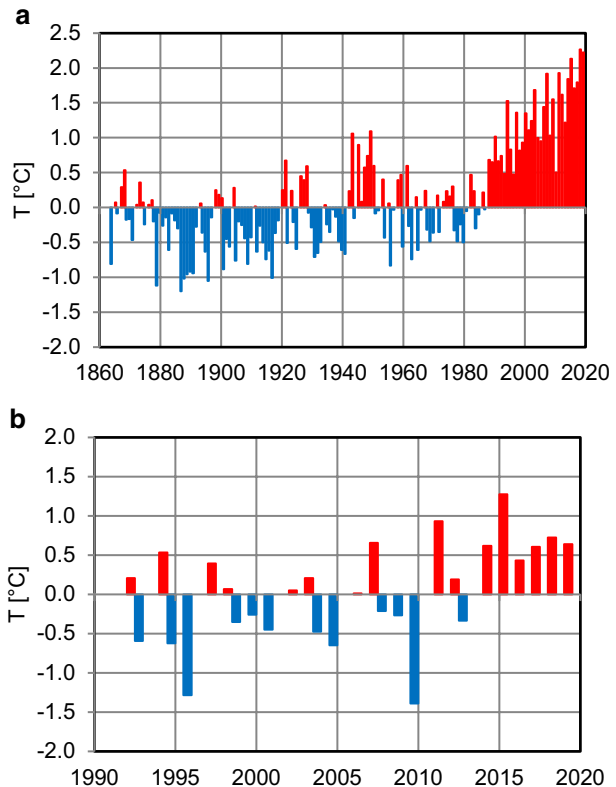
2.3 Monitoring of Lake and Inlet Waters and Deposition

Monitoring of Lake Leit started in the 1980s, first irregularly, after 2000 yearly (after snowmelt and in autumn) and since 2005 three times a year directly from the helicopter (after snowmelt and twice in autumn). The following chemical parameters have been measured in lake surface water: pH, conductivity at 20 °C (Cond), alkalinity (Alk), base cations (calcium (Ca), magnesium (Mg), sodium (Na), potassium (K)), ammonium (NH_4), sulfate (SO_4), nitrate (NO_3), chloride (Cl), reactive silica (Si) and after 2000 dissolved organic carbon (DOC) and trace metals.

In order to assess the possible role of atmospheric deposition on the long-term changes in the chemistry of Lake Leit, precipitation chemistry data collected at Robiei (see Fig. 1) between 1997 and 2018 were considered. Sampling occurred at weekly intervals with wet-only samplers. The collected rainwater and snow samples were analyzed for Cond, pH, Alk, base cations (BC), NH_4, SO_4 and NO_3. Yearly mean concentrations were calculated by weighting weekly concentrations with the sampled precipitation volume. Yearly mean Cond, pH, SO_4 and the sum of NO_3 and NH_4 (N_{in}) strongly correlated with values measured at Locarno Monti, a wet deposition sampling site with a longer data series and located at about 37 km south with respect to Robiei (see Fig. 1 for position). Therefore, Cond, pH and concentrations of SO_4 and N_{in} before 1996 were estimated from linear regression equations describing rainwater concentrations at

Robiei as a function of the concentrations measured at Locarno Monti. Intercept, slope and R-squared (R^2) of the linear regression equations were 2.85 μS cm^{-1}, 0.43, 0.76 for Cond; 1.84 μeq l^{-1}, 0.48, 0.75 for hydrogen ions (H); 3.04 μeq l^{-1}, 0.54, 0.87 for SO_4; and 9.32, 0.52, 0.57 for N_{in}.

To investigate the possible role of catchment-internal processes as possible causes for long-term changes in lake chemistry, we examined the slopes of the ionic relation ratio (Ca + Mg) versus SO_4, (Ca + Mg) versus HCO_3, HCO_3 versus SO_4 and Ca versus Mg in lake water to have insights into the stoichiometry of the weathering reactions. For this purpose, atmospheric corrected concentrations were used (*Ca, *Mg, *SO_4, *HCO_3). They were calculated by subtracting the annual mean concentrations in deposition from lake water concentrations. Moreover, two inflows and the outflow (I4, I5, Out, Fig. 2a) and three springs (I1, I2, I3, Fig. 2a) were sampled close to the lake border during baseflow conditions four times in autumn 2014, once in autumn 2015 and once in autumn 2017. Overall, the following parameters were determined: temperature (2015, 2017), Cond, pH, Alk. Si, Al, Cu, Zn (2014, 2017), BC, SO_4, NO_3, Cl (2014, 2015, 2017), DOC, Ni, Fe and the isotope δ^{34}S (2017). For the analyses of the data, concentrations of HCO_3 were estimated from the measured alkalinities (mostly equivalent in the studied surface waters).

2.4 Analytical Methods

With exception of the isotopes that were analyzed at the Stable Isotope Laboratory of the Geological Institute (ETH Zürich), all other chemical analyses were performed at the Laboratory of the Section for Air, Water and Soil Protection of the Canton of Ticino. pH, Alk, Cond were measured by means of potentiometric methods, Ca, Mg, Na, K, SO_4, NO_3, Cl by ion chromatography, NH_4, Si by continuous flow UV–VIS spectrophotometry, DOC by fusion UV/persulfate oxidation, trace metals by inductively coupled plasma-mass spectrometry. pH, Alk and Cond were measured in unfiltered samples, Ca, Mg, Na, K, SO_4, NO_3, Cl, Si after filtration through a cellulose acetate membrane filter with a pore size of 0.45 μm and DOC and transition metals after filtration through a polycarbonate membrane filter with a pore size of 0.40 μm. The laboratory regularly performs quality assurance (QA)/quality control (QC) programs. A comparison between the sum of anions and cations and between measured and calculated conductivity was performed for each analysis according to König et al. (2016). Further quality assurance measures adopted in the laboratory were the use of custom multi-analyte QC, certified and supplied by Inorganic Ventures, Christiansburg (USA) and the participation in inter-laboratory comparisons on surface water analysis, such as those organized within the ICP Waters (e.g., Escudero-Oñate 2018). More details on sampling and analytical procedures can be found in Steingruber and Colombo (2004, 2010).

For the analysis of sulfur isotope, about 1.6–1.8 l of sample was first acidified to a pH < 3 by addition of concentrated HCl. Afterward, SO_4 was precipitated as $BaSO_4$ by addition of 5 ml of a 1 M $BaCl_2 * 2H_2O$ solution. The solutions were then filtered with 0.45 μm cellulose acetate filters. The filters were washed with deionized water and dried at 70–80 °C. Sulfur isotope ratios (^{34}S/^{32}S) of $BaSO_4$ were analyzed by combustion–isotope-ratio-monitoring mass spectrometry (C–irmMS) at ETH Zürich as described in Bernasconi et al. (2017). Results are reported in the conventional δ-notation with respect to the Vienna Canyon Diablo Troilite (V-CDT).

3 Results

The thermal regime of the ground surface of the rock glacier, the daily snow cover and the daily mean air temperature at Robiei is shown in Fig. 4. The GST followed the typical thermal regime of a soil (Delaloye and Lambiel 2005; Ishikawa 2003), with short-term fluctuations linked to air temperature from late spring to autumn and attenuated short-term variations in the presence of sufficient snow. We observed a decrease in GST in late autumn and early winter as long as there was no or only a thin snow cover followed by a progressive stabilization of the GST as the snow cover reached sufficient depth for complete isolation reaching the WeqT. This was followed by a progressive increase when the snow cover started to thaw and by a 0 °C period during which melt water percolated to the ground. During the winters 2015/2016 and 2017/2018, the snow arrived only at the beginning of January or shortly before, while during the winter 2018/2019 a stable snow cover was reached already at the beginning of November attenuating the short-term variations. According to the WeqTs, the presence of permafrost is probable at site L1 (-4.6 °C and -4.4 °C in winter 2015/2016 and 2018/2019, respectively), possible at site L3 (-2.3 °C in winter 2015/2016) and unlikely at sites L2 (-1.5 °C, -1.5 °C, -1.0 °C in winter 2015/2016, 2017/2018 and 2018/2019, respectively) and L4 (-1.3 °C, -1.2 °C, -0.9 °C in winter 2015/2016, 2017/2018 and 2018/2019, respectively).

Lake Leit has average chemical characteristics comparable to other high-altitude alpine lakes (Rogora et al. 2013). Between 2016 and 2018, average autumn values/concentrations were Cond: 28 µS cm^{-1}, pH: 6.5, Alk: 34 µeq l^{-1}, Ca: 142 µeq l^{-1}, Mg: 56 µeq l^{-1}, Na: 22 µeq l^{-1}, K: 15 µeq l^{-1}, SO$_4$: 192 µeq l^{-1}, NO$_3$: 11 µeq l^{-1}, Cl: 3 µeq l^{-1}, Si: 34 µmol l^{-1}, DOC: 0.53 mg l^{-1}, Al: 5 µg l^{-1}, Cu: 0.33 µg l^{-1}, Zn: 0.95 µg l^{-1}. Only concentrations of Ni (5.6 µg l^{-1}, average 2016–2018) were slightly higher compared to other lakes in the region (Steingruber 2019).

Figure 5 shows the temporal evolution of the chemistry of rain- (Robiei) and lake water (Lake Leit) from the early 1980s to the present. Rainwater Cond and concentrations of SO$_4$, of inorganic nitrogen (N$_{in}$ = NO$_3$ + NH$_4$) decreased. In contrast, as a consequence of the decreasing concentrations of the acidifying pollutants SO$_4$ and NO$_3$, rainwater pH increased. Concentrations of SO$_4$ in lake water were in the same range as measured in rainwater in the early 1980s but increased by a factor 4 particularly after 2010. Similarly, concentrations of Ca + Mg increased by a factor 3. Concentrations of pH, HCO$_3$, Na, K and Si also increased but not as strongly as Ca + Mg and SO$_4$. The much lower concentrations of N$_{in}$ in lake water compared to rainwater are due to nitrogen retention in the
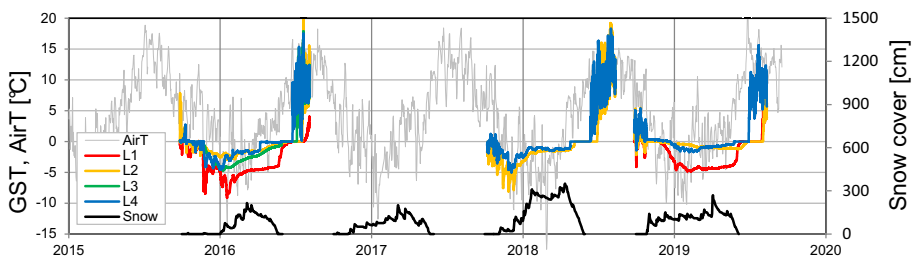

Fig. 4 Daily mean air temperature (AirT), daily snow cover (Snow) at Robiei and ground surface temperature (GST) of the rock glacier in the Lake Leit catchment
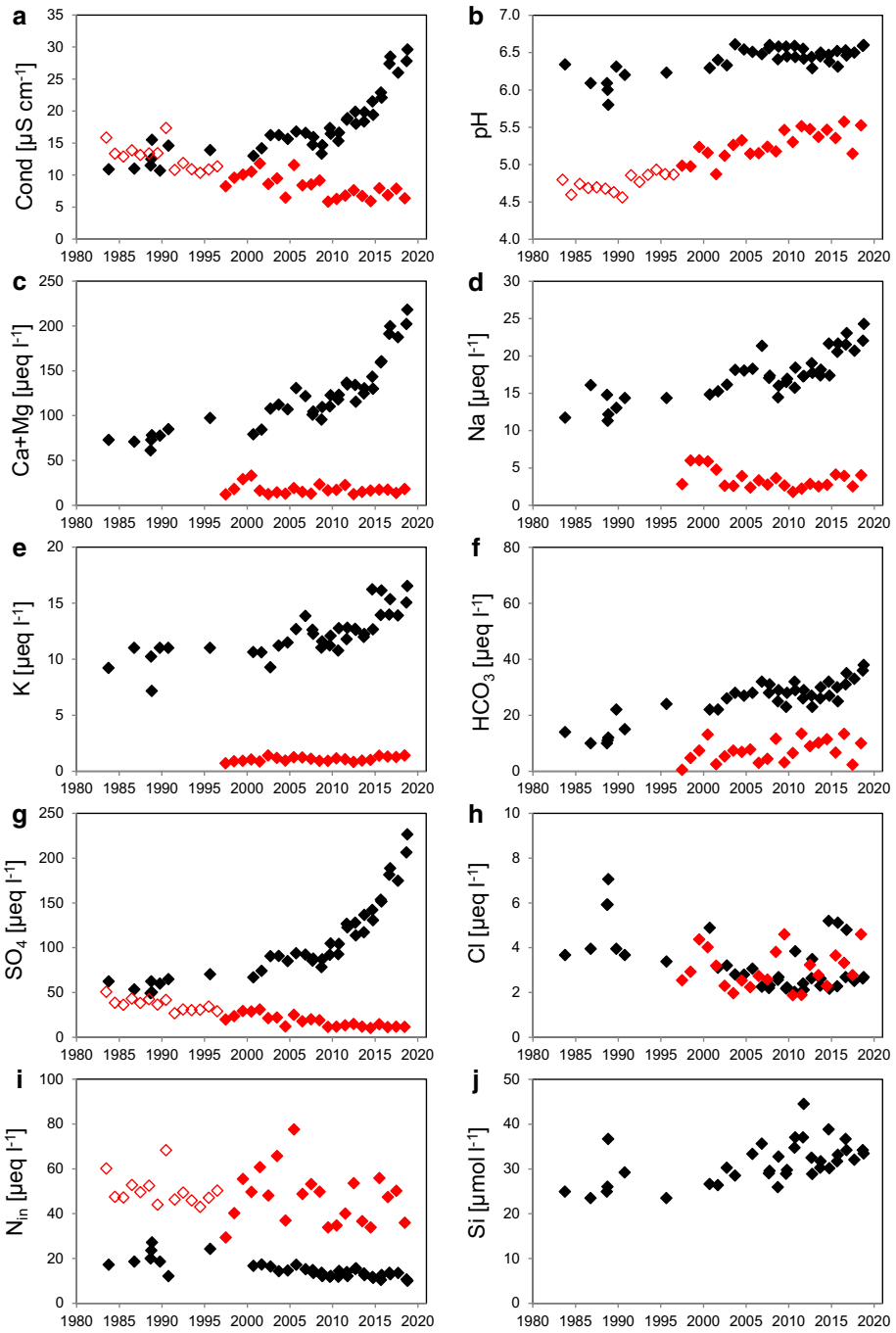
Fig. 5 Cond, pH, Ca+Mg, Na, K, HCO₃, SO₄, Cl, N_in, Si in rainwater at Robiei (annual mean, red diamonds) and in Lake Leit (autumn samples, black diamonds). The open red diamonds are estimated values

catchment (denitrification, assimilation). In contrast, the much higher concentrations of SO_4, $Ca + Mg$, Na and K in lake water compared to rainwater suggest sources in the catchment. Cl concentrations in atmospheric precipitation and in lake water of lake Leit were in the same order of magnitude. Since Cl is a conservative ion and sources of Cl in the catchment are not known, this correspondence suggests that rainwater chemistry measured at Robiei is a fairly good indicator for rainwater chemistry in the Lake Leit catchment. Time series of concentrations of DOC, aluminum (Al), copper (Cu), zinc (Zn) did not show significant trends.

Figure 6 presents the water chemistry of the inlets and the outflow of Lake Leit in autumn 2014, 2015 and 2017. Considering Cond, $Ca + Mg$ and SO_4, the parameters characterized by the highest increase during the monitoring period, it can be observed that I1 had the lowest concentrations, even lower than Out, I2 had concentrations similar to Out, while I3, I4 and I5 had higher concentrations than Out. Among these, I3 and I4, the inlets probably most influenced by the rock glacier, had the highest concentrations (up to 56 µS cm^{-1} of Cond, 324 µeq l^{-1} of Ca, 146 µeq l^{-1} of Mg and 513 µeq l^{-1} of SO_4). I4 and I3 also displayed the highest concentrations of Na and K. Concentrations of HCO_3 were low (< 50 µeq l^{-1}) and similar at the sampled sites. Only in autumn 2017 concentrations of HCO_3 higher than average were measured at I4 and lower than average at I1. pH was always around 6.5 at all sites, with exception of I1 that was characterized by lower values (between 5.5 and 6.0). NO_3 was always below the annual mean concentrations of N_{in} in rainwater (40–60 µeq l^{-1}) at all sites. However, concentrations were higher in the inlets draining bare land (I2, I3, I4) compared to those draining partially vegetated land (I1, I5) (see Fig. 2a), probably because of N uptake by vegetation. Concentrations of trace metals and DOC were low, but differences among the different sites were detected (Table 1). Concentrations of Al, Cu, Zn were highest at I1, the inlet with the lowest pH (5.7–6.0). Differently, concentrations of Ni were elevated at I3, I4, I5, the spring and inflows influenced by the rock glacier. DOC was highest at I1, probably because of the presence of vegetation.

Figure 7 shows a Piper diagram (Piper 1944), indicating that Lake Leit was dominated by $Ca + Mg$ and SO_4. Compared to the average lake water composition of the BC before 2010, after 2010 the contribution of Ca remained stable (60%), while that of Mg slightly increased (from 10 to 13%) at the expense of Na and K. As a consequence, the average Ca/Mg ratio decreased slightly from 3.4 to 2.8. The dominance of SO_4 in the anions increased from 71 to 78%. Similar to lake water, inflows and springs were also dominated by Ca, Mg and SO_4. However, as observed for the absolute chemical concentrations, the springs/inflows differentiate from each other also as regards their relative concentrations. They can be divided into three groups: I3, I4 and I5, draining the southwestern part of the catchment, with maximum contributions of $Ca + Mg$ (from 62 to 68%) and of SO_4 (from 83 to 90%), I2, draining the southeastern part of the catchment, with intermediate contributions of $Ca + Mg$ (from 60 to 64%) and of SO_4 (from 75 to 80%) and I1, draining the eastern part of the catchment, with smallest contributions of $Ca + Mg$ (from 48 to 50%) and SO_4 (from 64 to 77%) instead of higher contributions of Na (from 27 to 30%) and HCO_3 (from 22 to 35%). The lowest Ca/Mg ratios were observed in I3, I4, I5 (mean 2.9), intermediate values at I2 (3.1) and highest at I1 (3.3).

The plots in Fig. 8 show the ionic relation ratio [$*(Ca + Mg)$ vs. $*SO_4$], [$*(Ca + Mg)$ vs. $*HCO_3$], [$*HCO_3$ vs. $*SO_4$] and [$*Ca$ vs. $*Mg$] in lake water (Fig. 8a–d). The temporal change in the concentrations of $*(Ca^{2+} + Mg^{2+})$ was significantly related to changes in concentrations of $*SO_4$ and $*HCO_3$ (Fig. 8a, b, respectively), whereas the slope of the linear regression in Fig. 8a close to one indicates that the changes in concentrations of $*(Ca^{2+} + Mg^{2+})$ were mainly related to changes in concentrations of $*SO_4$. In addition,

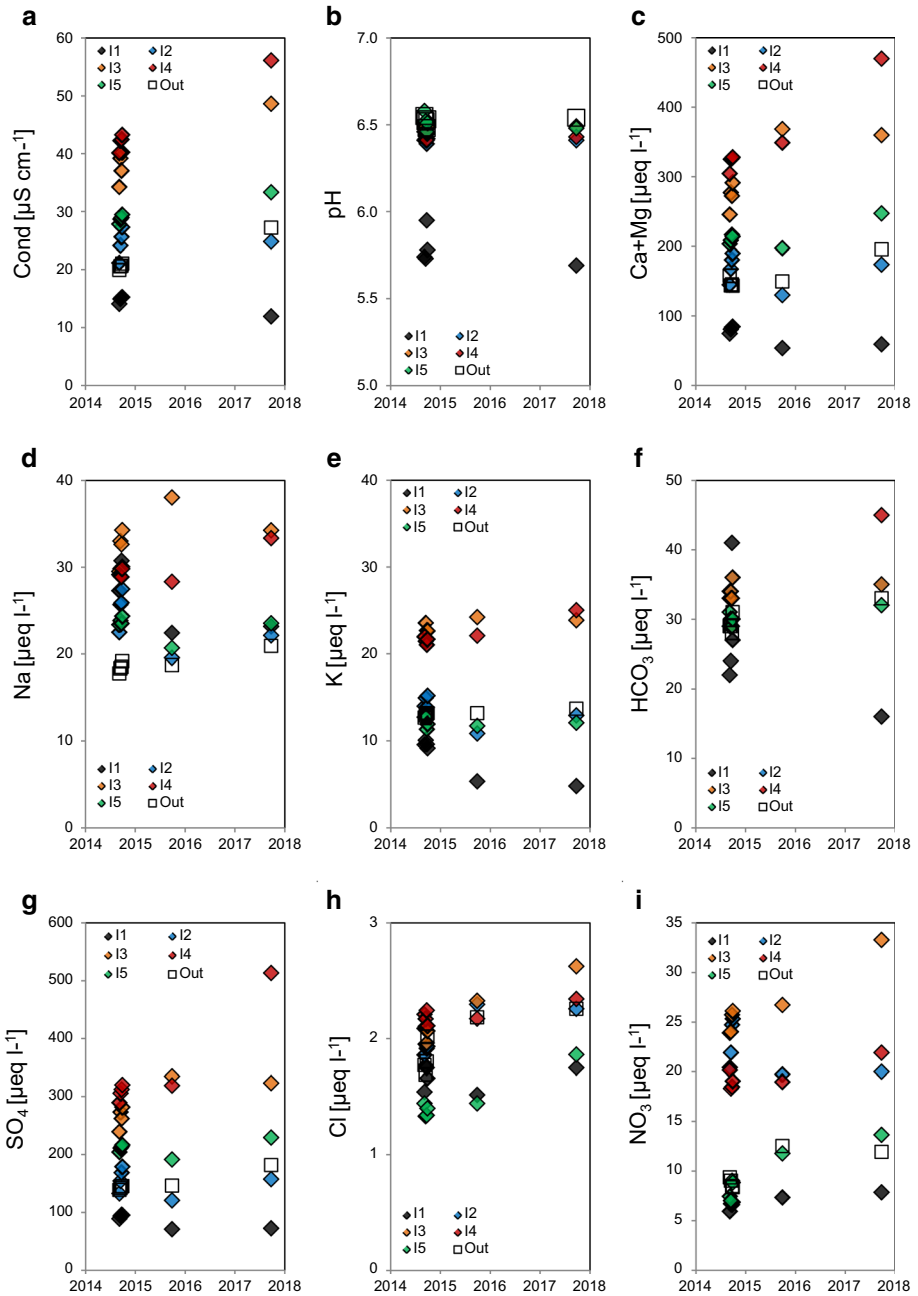**Fig. 6** Cond, pH, Ca + Mg, Na, K, HCO₃, SO₄, Cl, NO₃ measured in autumn 2014 and 2017 and Ca + Mg, Na, K, SO₄, Cl, NO₃ measured in autumn 2017 in the inlets (I1–I5) and the outflow (out) of Lake Leit

Table 1 Chemical parameters and their limit of quantification (LOQ) measured in the lake inlets and the outflow

	LOQ	I1	I2	I3	I4	I5	Out
Cond (μS cm^{-1})	1.0	14 ± 1	25 ± 2	40 ± 5	45 ± 6	30 ± 2	22 ± 3
pH	0.02	5.8 ± 0.1	6.4 ± 0.0	6.5 ± 0.0	6.4 ± 0.0	6.5 ± 0.0	6.5 ± 0.0
Alk (μeq l^{-1})	1.0	26 ± 9	34 ± 1	34 ± 1	33 ± 7	30 ± 1	30 ± 2
Ca (μeq l^{-1})	1.4	55 ± 10	126 ± 17	225 ± 34	252 ± 36	163 ± 13	114 ± 14
Mg (μeq l^{-1})	0.5	18 ± 3	38 ± 5	78 ± 16	98 ± 24	51 ± 5	42 ± 8
Na (μeq l^{-1})	0.4	27 ± 4	24 ± 3	34 ± 3	30 ± 2	23 ± 1	19 ± 1
K (μeq l^{-1})	2.0	8 ± 2	14 ± 2	23 ± 1	22 ± 1	12 ± 1	13 ± 0
SO$_4$ (μeq l^{-1})	0.2	86 ± 12	152 ± 22	286 ± 37	343 ± 84	211 ± 13	150 ± 16
NO$_3$ (μeq l^{-1})	0.7	7 ± 1	22 ± 2	27 ± 3	19 ± 1	10 ± 3	10 ± 2
Cl (μeq l^{-1})	0.06	2 ± 0	2 ± 0	2 ± 0	2 ± 0	1 ± 0	2 ± 0
Si (μmol l^{-1})	0.1	73 ± 8	54 ± 5	59 ± 5	64 ± 4	55 ± 4	35 ± 3
DOC (mg l^{-1})	0.2	0.5	0.3	0.3	0.3	0.3	0.5
Al (μg l^{-1})	1.0	27.1 ± 8.0	3.0 ± 0.6	3.9 ± 2.6	1.9 ± 0.5	4.0 ± 1.6	11.1 ± 3.2
Cu (μg l^{-1})	0.1	0.3 ± 0.1	0.2 ± 0.2	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.4 ± 0.3
Zn (μg l^{-1})	0.1	2.5 ± 0.5	0.7 ± 0.1	0.4 ± 0.2	0.5 ± 0.2	0.4 ± 0.1	1.1 ± 0.9
Ni (μg l^{-1})	0.1	0.1	0.6	8.4	18.3	6.5	6.2
δ^{34}S (‰)	0.2	13.6	13.2	13.9	15.2	14.1	13.8

For Cond, pH, Alk. Si, Al, Cu, Zn, the values represent the average and the standard deviation of the 2014 and 2017 autumn samples, for Ca, Mg, Na, K, SO$_4$, NO$_3$, Cl the average and the standard deviation of the 2014, 2015 and 2017 autumn samples and for DOC, Ni and δ^{34}S the values measured in the 2017 autumn sample

Fig. 8c indicates that concentrations of *HCO$_3$ were related to concentrations of *SO$_4$ and that before and after 2010 the increase in the concentrations of *SO$_4$ occurred at a five and 14 times higher rate, respectively, than that of the concentrations of *HCO$_3$. Similarly, Fig. 8d shows also the very good correlation between *Ca and *Mg and that after 2010 concentrations of *Mg increased at a higher rate than concentrations of *Ca.

Interestingly, SO$_4$ concentrations in the springs and the inflows correlated negatively with water temperature (Fig. 9a). Low temperatures are here probably indicators for the extent the springs/inflows are influenced by permafrost. At the same time, SO$_4$ concentrations in the springs and the inflows correlated positively with δ^{34}S (Fig. 9b). Because of the small number of data, however, the relation is statistically not significant. Nevertheless, the relationship suggests that δ^{34}S values are higher at the sites most impacted by permafrost. δ^{34}S varied between 13.6 and 15.2‰ in the springs and inflows and was 13.8‰ in the outflow (Table 1).

4 Discussion

Changes in rainwater chemistry reflect the Europe-wide efforts of the last 30–40 years to reduce anthropogenic emissions of pollutants, particularly of sulfur (sulfur dioxide) and nitrogen (nitrogen oxides and ammonia) (Koolen and Rothenberg 2019). The water chemistry of Lake Leit also changed considerably during the last 35 years: Cond, Ca, Mg, Na,
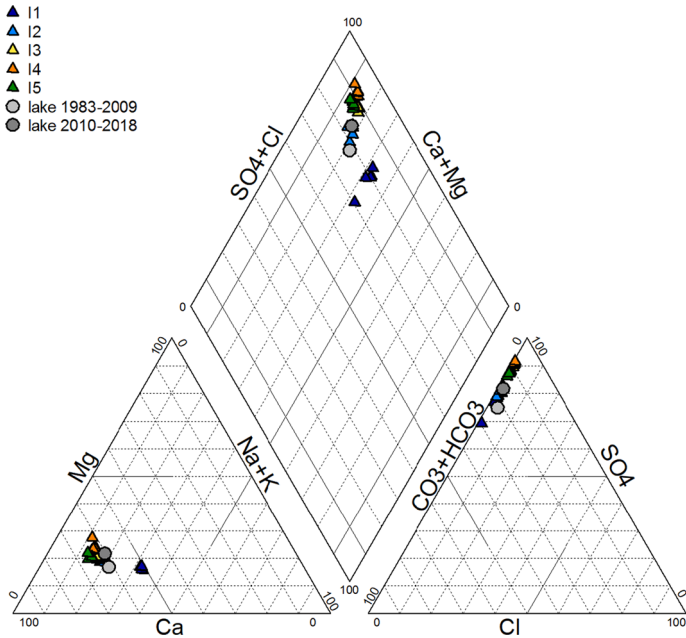
Fig. 7 Piper diagram of the inlets sampled in autumn 2014, 2015 and 2017 and of Lake Leit represented by average autumn values for the periods 1983–2009 and 2010–2018
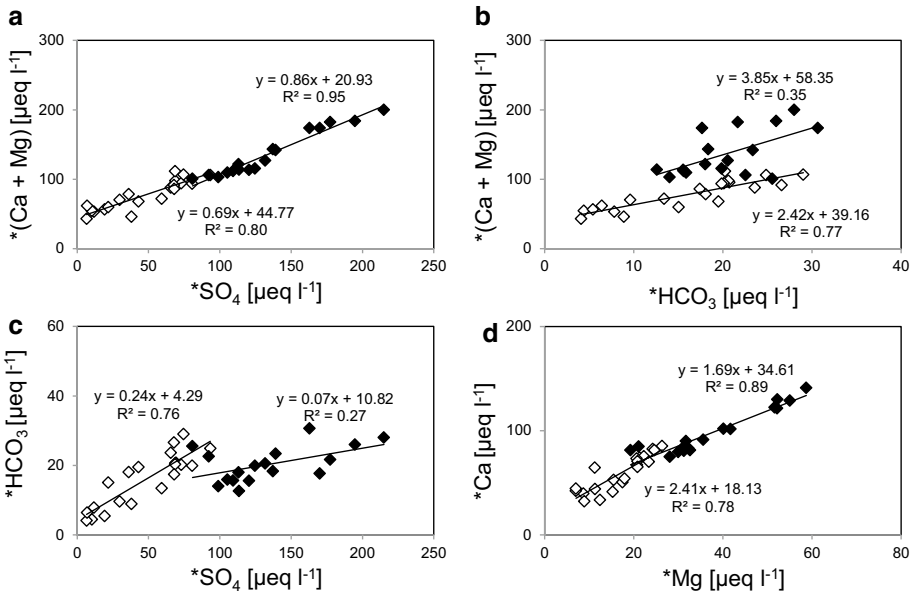

Fig. 8 Lake water ionic ratios [*(Ca+Mg) vs. *SO_4] (**a**), [*(Ca+Mg) vs. *HCO_3] (**b**), [*HCO_3 vs. *SO_4] (**c**) and [*Ca vs. *Mg] (**d**). Open and black diamonds represent autumn concentrations of the periods 1983–2009 and 2010–2018, respectively. * indicates atmospheric corrected concentrations
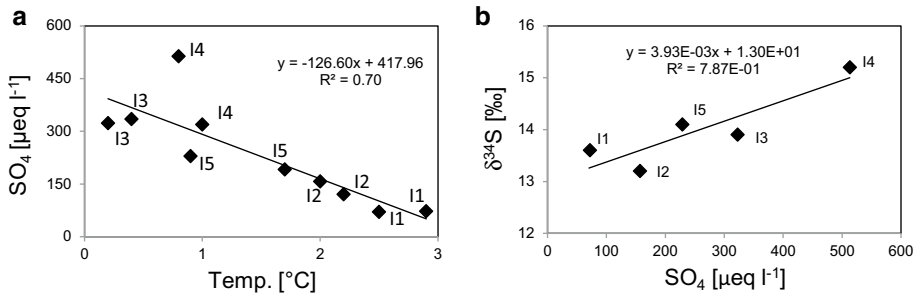
Fig. 9 Temperature dependence of SO_4 concentrations measured in the springs and inflows in autumn 2015 and 2017 (**a**) and dependence of SO_4 concentrations from $\delta^{34}S$ measured in the springs and inflows in autumn 2017 (**b**)

K, SO_4, HCO_3, pH increased, while NO_3 decreased. The increase in HCO_3 and pH and the decrease in NO_3 are a well-known phenomenon caused by the decrease in the emissions into the atmosphere of acidifying pollutants (Garmo et al. 2014; Rogora et al. 2013). In contrast, the increase in conductivity, base cations and SO_4 cannot be attributed to changes in atmospheric deposition. The opposite is normally observed in high-altitude alpine lakes (Garmo et al. 2014; Rogora et al. 2013). The fact that concentrations of BC and SO_4 increase in lake water but decrease in rainwater, the only relevant catchment external source, indicates the existence of a BC and SO_4 source in the catchment that has increased in importance during the last decades, following an exponential increase particularly from the early 2000s onward. Similar simultaneous trends have been reported for high mountain lakes elsewhere in the Central Alps, e.g., in Lake Rasass (Italy) and in Schwarzsee ob Sölden (Austria), which have become impacted by climate warming-induced rock glacier melt waters (Thies et al. 2007). The recent water chemistry measurements of the main inlets confirmed the presence of catchment internal sources of BC and SO_4: up to twice the concentrations in the outlet were measured in the spring and the inflow draining the southern part of the catchment (I3, I4), where the rock glacier is situated and the presence of permafrost has been shown to be very probable. In addition, highest concentrations of SO_4 and base cations were found in the spring/inflows with coldest temperature, a probable indicator of the extent of the permafrost influence. These results together with the climate warming occurring in the study area, since early 2000s, suggest that the observed increase in base cations and SO_4 in lake water is most probably related to the climate warming-induced thawing of the permafrost in the rock glacier. Indeed, numerous studies have observed increasing rock glacier surface velocities potentially in response to recent climate warming (Jones et al. 2019). For the European Alps, a mean surface velocity increase of +52% relative to the respective previous year has been reported for the investigated period (2010–2014, PERMOS 2016).

"Old SO_4" trapped in the rock glacier ice originating from the period when deposition of sulfuric acid was highest (around the 1980's, Rogora et al. 2016) is not a likely source, because concentrations in rainwater at Lake Leit have never been as high as they are presently in the lake water. Thus, a geogenic source is more likely. In the Alpine region, dissolved SO_4 originates mainly from dissolution of gypsum ($CaSO_4 \cdot 2H_2O$) and/or anhydrite ($CaSO_4$) and from oxidative dissolution of sulfide-bearing minerals (e.g., pyrite) (Dubois et al. 1993; Pastorelli et al. 2001; Strauss et al. 2015; Vuataz 1982). The slope of the lake water [*(Ca+Mg) vs. *SO_4] ionic relation ratio close to 1 is consistent with either

dissolution of gypsum/anhydrite or oxidation of sulfide coupled to weathering of calcium silicates (Auqué et al. 2019; Stachnik et al. 2016; Tranter et al. 2002). The position of I3, I4 (the inlets most influenced by the rock glacier) and I5 in the Piper Diagram (Fig. 7) suggests gypsum/anhydrite as the main cations and anions source (100% Ca and 100% SO_4; Spence and Telmer 2005). Oxidation of sulfide is less probable because an increase in SO_4 concentrations would have been coupled with a decrease in pH unless the produced acidity had been buffered by weathering of either silicate or carbonate. However, according to Spence and Telmer (2005), the weathering of silicates would probably have produced a greater contribution of Na and K to the cations and weathering of carbonates a greater contribution of bicarbonate to the anions. In addition, sulfide oxidation coupled to carbonate dissolution produces slopes of [(Ca + Mg) vs. SO_4] of 2 (Tranter et al. 2002) and not close to 1 as observed in this study. A further confirmation of the geological origin of SO_4 comes from the analyses of sulfur isotopes: indeed, $\delta^{34}S$ in the outlet of the lake (13.8‰) and in the inlets (13.6–15.2‰) is in the range reported for marine evaporites from the Middle Triassic (Bernasconi et al. 2017) or from barite occasionally found in fracture fillings in crystalline basements. Balderer et al. (1991) reported $\delta^{34}S$ values of 11–16‰ for barite from the crystalline of deep boreholes in Northern Switzerland. However, weathering of barite would not produce a significant coupling between Ca and SO_4. On the other hand, the $\delta^{34}S$ composition of pyrite from crystalline rocks in Switzerland is generally around zero (Balderer et al. 1991; Hartmann 1998). The correlation of $\delta^{34}S$ with concentrations of SO_4 indicates that in the spring/inflows most influenced by the rock glacier (I3, I4, I5), characterized by higher concentrations of SO_4 and lower temperatures, the SO_4 is almost exclusively derived from gypsum/anhydrite, while in the other inlets, a small part of SO_4 probably originates from the oxidation of pyrite. According to these results, gypsum/anhydrite must be present in trace amounts in the whole lake catchment not only in the rock glacier area. Interestingly, the Geologic Atlas of Switzerland 1:25.000 (Swisstopo 2015; see Fig. 2) does not confirm the ubiquitous presence of gypsum/anhydrite in the catchment. The lake is indeed crossed by a narrow band of Triassic metasediments, but constituted by sericite quartzite (Bianconi 1971) and only at the eastern side, immediately outside of the catchment, the presence of lenses of dolomite marble has been reported (Bianconi 1971). However, because of the measured $\delta^{34}S$ values and the proximity of the lake to the large Triassic Campolungo area, the presence of subsurface veins of Triassic dolomite with traces of evaporites in the catchment cannot be excluded. Other conceivable sources are slices of anhydrite of probably Triassic origin in gneiss as found in the Leventina nappe about 12 km far from the study site (Hiss 1975).

Assuming that all the SO_4 in Lake Leit originates from a mixture of Triassic evaporites and pyrites (the contribution from precipitation can be quantitatively neglected, see Fig. 5g) and assuming typical $\delta^{34}S$ values of 15‰ for the first and 0‰ for the second, then the relative contributions of evaporites ($X_{Evaporite}$) and pyrite ($X_{Evaporite}$) in the inlet and the outflow samples of 2017 can be calculated by mass balance according to:

$$\delta^{34}S_{Sample} = X_{Pyrite} \cdot \delta^{34}S_{Pyrite} + X_{Evaporite} \cdot \delta^{34}S_{Evaporite} \tag{1}$$

and

$$X_{Evaporite} = 1 - X_{Pyrite} \tag{2}$$

$X_{Evaporite}$ and X_{Pyrite} of 2017 samples are then 91% and 9% for I1, 88% and 12% for I2, 93% and 7% for I3, 100% and 0% for I4, 94% and 6% for I5, 92% and 8% for Out. Relative contributions of evaporites and pyrite to the lake SO_4 can also be estimated from the

ionic relation ratios presented in Fig. 8. Assuming that all *HCO_3 correlating with *SO_4 has been produced by sulfide oxidation coupled to carbonate dissolution, from the slopes of the ionic relation ratio[*HCO_3 vs. *SO_4] and according to the theoretical weathering equations of sulfide oxidation coupled to carbonate dissolution (Stachnik et al. 2016; Tranter et al. 2002), it can be derived that for 1.0 meq l^{-1} of SO_4, 0.24 meq l^{-1} of *HCO_3 and 0.48 meq l^{-1} of *(Ca+Mg) were produced during 1983–2009 and 0.07 meq l^{-1} of *HCO_3 and 0.14 meq l^{-1} of *(Ca+Mg) during 2010–2018. Subtracting these amounts of *(Ca+Mg) from the slope of the ionic relation ratio*(Ca+Mg) versus *SO_4, we obtain the amount of *(Ca+Mg) and *SO_4 involved in sulfate dissolution (0.45 meq l^{-1} during 1983–2009 and 0.79 meq l^{-1} during 2010–2018). The remaining *SO_4 (0.31 meq l^{-1} during 1983–2009 and 0.14 meq l^{-1} during 2010–2018) can be attributed to sulfide oxidation coupled to weathering of calcium and magnesium containing silicate. In other words, during 1983–2009, 45% of the *SO_4 in the lake may have originated from sulfate dissolution, 31% from sulfide oxidation coupled to weathering of calcium and magnesium containing silicate and 24% from sulfide oxidation coupled to carbonate dissolution (=55% from oxidation of pyrite), and during 2010–2018 79% from sulfate dissolution, 14% from sulfide oxidation coupled to weathering of calcium and magnesium containing silicate and 7% from sulfide oxidation coupled to carbonate dissolution (=21% from oxidation of pyrite). This result suggests that the increase in concentrations of *SO_4 has gone along with an increase in the contribution from sulfate dissolution and is consistent with the estimations made from the recent $\delta^{34}S$ measurements in the inlets and the outflow.

The cause of the observed increased weathering of SO_4-bearing minerals below the rock glacier is not clear. Highest concentrations of solutes in rock glacier springs normally occur in late summer and early autumn during baseflow conditions (Baron et al. 2009; Thies et al. 2013; Williams et al. 2006), when the dilution effect of melting snow and rainwater is minimal. According to a model proposed by Giardino et al. (1992) and consistent with the conclusions of Krainer and Mostler (2002), subsurface flow occurs as quickflow atop and as baseflow below the frozen body of the rock glacier, respectively. The first is mainly derived from intense snowmelt or heavy rainfall events, and the second seems to be supplied by slow diffuse groundwater that flows through the unfrozen, fine-grained material at the base of the rocks glacier. The contribution of ice melt to the total rock glacier discharge seems to be minimal (Jones et al. 2019). Increased concentrations of solutes in rock glacier springs during baseflow have been associated with the longer residence time and rock–water interaction and the abundance of freshly exposed mineral surfaces caused by permafrost thaw (Colombo et al. 2018). This would also explain the general temporal increase in the weathering rates of the cations (Ca, Mg, K, Na) and most anions (SO_4, HCO_3), but also the higher increase in the weathering rates of SO_4 compared to HCO_3 and of Mg compared to Ca. Triassic dolomite metasediments that are known to be associated with evaporites are present in the surroundings of Lake Leit. If they are present in the underground in the catchment, their exposure to water induced by permafrost thaw would initially increase the overall weathering rates and shift the relative ionic composition in the discharge toward those ions that originate from the more soluble minerals. That means in the opposite order that normally characterizes seawater precipitation during the formation of evaporite: first the most soluble $MgSO_4$, then $CaSO_4$ and at least dolomite ($CaMg(CO_3)_2$) (Balzer 2003).

The hydrochemistry of the rock glacier springs analyzed in this study is consistent with that reported for other rock glacier outflows or rock glacier impacted surface waters: clear waters with increased conductivity and generally enriched with Ca, Mg, SO_4 (Fegel et al. 2016; Nickus et al. 2015; Rotta et al. 2018; Thies et al. 2007; Williams et al. 2006). With

respect to HCO_3, rock glaciers can induce enrichment (Colombo et al. 2019; Fegel et al. 2016; Lecompte et al. 2008), depletion (Ilyashuk et al. 2014; Thies et al. 2013) or neither/nor (Rotta et al. 2018; Williams et al. 2006) depending on the geologic composition of the catchment. In the Austrian Alps, rock glacier thaw in catchments with sulfide-bearing bedrock affected acid rock drainage producing acidic metal-rich waters exceeding the EU limit for Ni in drinking water (20 µg l^{-1}) by a factor of 10 (Thies et al. 2007, Thies et al. 2013). The origin of this Ni is still uncertain: Krainer et al. (2015) determined high heavy metal concentrations in a rock glacier ice core not explainable with the surrounding lithology. In this study, a similar dramatic increase in metal concentrations was not observed. However, although the spring and the inflows influenced by the rock glacier (I3, I4, I5) and Lake Leit were not acidic, they were enriched with Ni (6.2–18.3 µg l^{-1}), while the other measured metals, particularly Al and Zn, were according to the pH low. In fact, most mountain Alpine lakes in the region have concentrations of Ni $\leq$ 0.2 µg l^{-1} (Steingruber 2019). In contrast, the springs not influenced by the rock glacier (I1, I2) had both low Ni (0.1 µg l^{-1}) values, while Al and Zn were coherent to their pH elevated in I1 (pH < 6.0) and low in I2 (pH > 6.0).

With respect to the origin of the SO_4 discharged by rock glaciers, most studies hypothesized oxidation of sulfide (Ilyashuk et al. 2018; Williams et al. 2006; Thies et al. 2017) or dissolution of gypsum generated by sulfide oxidation (Lecompte et al. 2008), because of the ubiquitous presence of pyrite in metamorphic rocks. Discharge of SO_4 as a consequence of gypsum or anhydrate dissolution has been reported less frequently (Colombo et al. 2019; Rogora et al. 2020). However, the distinction between different geological sources is not easy and is often possible only with a detailed analyses of the lithology and/or the S and O isotopes of sulfate.

Some studies also reported that surface waters influenced by rock glaciers are characterized by higher NO_3 concentrations compared to those not influenced by rock glaciers (Barnes et al. 2014; Williams et al. 2007) and attributed it to the presence of nitrifying microorganisms in the interior of the rock glacier. In addition, a temporal increase in nitrate concentrations in rock glacier-impacted surface waters has also been occasionally observed (Baron et al. 2009). In this study, concentrations of NO_3 in Lake Leit did not increase with time; on the contrary, it decreased following the trend of atmospheric deposition. However, compared to the inlets not influenced by the rock glacier, those impacted by the rock glacier clearly showed higher NO_3 concentrations, but since average rainwater N concentrations were in the same range, if not higher, according to the N mass balance, the rock glacier cannot be considered a N source. Instead, the different N concentrations in the lake inlets may be explained by different N retention rates with lower values below the unvegetated rock glacier subcatchment.

5 Conclusion

In this study, we show that rock glacier thaw enhanced weathering of probably fresh exposed evaporite minerals increasing the BC and SO_4 concentrations in a mountain Alpine lake by a factor of 3 and 4, respectively, during the last 40 years. In terms of Swiss drinking water criteria, the concentrations of SO_4 are still far below (factor 25) the highest accepted limit (250 mg l^{-1}) and the measured conductivity is still typical of very soft waters. However, concentrations of Ni are approaching the maximum accepted limit in Switzerland in one lake inlet (20 µg l^{-1}). Therefore, lake water concentrations, if used for drinking water purpose, should be monitored.

Compared to other mountain lakes in the region, Lake Leit represents an exception. A first look at other 19 regularly and 31 occasionally monitored sites (Steingruber 2018) showed that an increase in BC and SO_4 occurred only in three regularly and two occasionally monitored lakes. Similar to Lake Leit, all other five lakes are characterized by a high probability of permafrost occurrence in their catchment. However, the extent of the ion increase is much less dramatic than observed in Lake Leit, probably because of the much larger relative catchment area occupied by the rock glacier in the latter (10%). Lake Morghirolo, for instance, the lake with the second largest rock glacier to catchment area (2.9 times smaller than that of lake Leit), is characterized by a three times lower increase in sulfate. The relevance of the rock glacier to catchment area is also suggested by the results of Thies et al. (2007): in lake Rasass, which has a 3.5 higher rock glacier-to-catchment area ratio than lake Schwarzsee ob Sölden, sulfate concentrations increased by a 4.5 higher rate. An increase in the weathering rates, even if smaller, may have occurred in other lake catchments as well, but may not have produced an increase in concentrations of the weathered ions in the lakes, because compensated by the decrease in atmospheric SO_4 deposition.

A more detailed data analysis is required to estimate the extent of the effects of permafrost thaw on surface water chemistry in high-alpine setting. Further research is also needed to understand the dynamics of this phenomena, for example the time necessary to reach maximum weathering activity and the long-term impact on water quality.

Data Availability The presented data have not been deposited in a public repository.

Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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