Temporal dynamics in the physico-chemistry of a high-alpine stream network in the Swiss National Park

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Abstract

The Macun lakes form a high-alpine (> 2,600 m asl) cirque landscape (3.6 km^2) in the Swiss National Park, comprising 26 small lakes together with a number of temporary ponds. Streams interconnect the four largest lakes, forming the drainage network that flows into the Inn River at the town of Lavin. The drainage network of Macun consists of a north and a south basin that overlie an ortho-gneiss, meta-granitoid bedrock. The south basin is influenced by various rock glaciers. The physico-chemistry of surface waters at 10 sites has been monitored annually in mid-summer since 2001. Further, an YSI EXO2 Multiparameter Sonde (Exosonde) with various water quality sensors has been employed since 2016 at the last lake in the network to examine seasonal and diel patterns in physico-chemistry. Results showed clear physico-chemical differences between the two basins, which mostly reflect rock-glacier inputs in the south basin. Nitrogen values were two-fold higher and particulate phosphorus values two-fold lower in the south basin than in the north basin. Over time, the physico-chemistry in the two basins became more homogeneous, with a reduction in rock-glacial inputs in the south basin and an overall decrease in nitrogen in the catchment. Data from 30 springs and tributaries sampled in 2002 and 2017 reflected the basin differences and temporal changes observed at the primary study sites. Continuous temperature records showed north basin streams to be ca. 3°C warmer than south-basin streams, but with high inter-annual variation that reflected annual differences in weather and no evidence of a general change over time (increase or decrease). Exosonde data revealed strong seasonality in measured parameters as well as seasonality in diel patterns (e.g., dissolved oxygen, temperature, chlorophyll-a); diel fluctuations were most pronounced in summer and least in winter. The results highlight the importance of long-term monitoring for understanding ecosystem state changes in alpine freshwaters, especially during periods of rapid environmental change.

Profile

Protected area

Swiss National Park

Mountain range

Alps

Country

Switzerland

Introduction

High-elevation environments are sentinels of climate change (Federal Office of the Environment (FOEN) 2021). These alpine landscapes house the glaciers of the world, most of which have been receding rapidly over recent decades under a warming climate (IPCC 2013). Alpine surface waters, comprising both standing and running waters, have experienced changes in physico-chemistry in response to climate-induced alterations in water inputs (quantity, quality and timing) (Scherrer et al. 2016; Brunner et al. 2019). In particular, alterations in water inputs act concomitantly with changes in the seasonal patterns of precipitation. For instance, most of the winter snowfall in the European Alps now occurs later in the season, sometimes as spring precipitation events, and most areas experience extreme drying in late summer followed typically by autumn increases in precipitation (FOEN 2021). In fact, flow intermittency in late summer affects a high proportion (up to 90%) of tributary streams in alpine landscapes (Robinson & Matthaei 2007; Paillex et al.

2020). Lastly, over time, human-related environmental changes also have caused some degree of change in atmospheric deposition of certain trace substances and pollutants. For example, nitrogen deposition in some areas of the European Alps has decreased due to changes in industrial activities in neighbouring countries (Rogora et al. 2006; Magnuz et al. 2017).

Rock glaciers are common landforms associated with high-mountain periglacial landscapes such as the Macun cirque. Rock glaciers comprise a mix of debris (e.g. talus) and ice, and typically move slowly downwards into valleys. Rock-glacier movement is seasonal, beginning with snowmelt in spring, with highest velocities in summer; movement can be particularly rapid after intense rainfall. However, rock glaciers globally have been moving faster in recent decades due to climate change (Kenner et al. 2020). For example, the horizontal displacement of the large rock glacier in Macun has increased markedly since 1988 (Zick 1996; Barsch & King 1998; Fehr & Reich 2015). Rain and meltwater can penetrate rock glaciers more easily today because ice has become warmer with climate
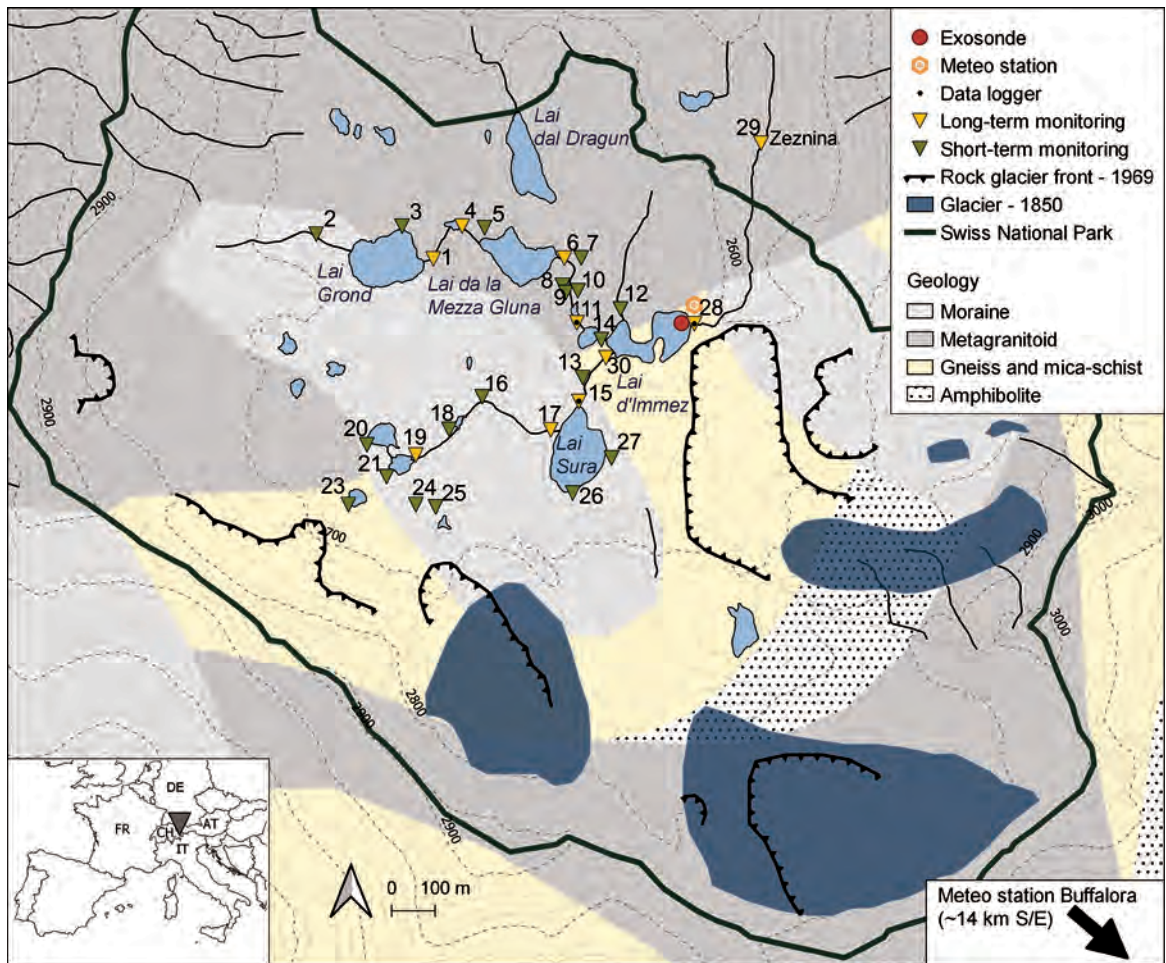
Figure 1 – Map of the Macun Lakes area. Note the rock glaciers that influence the hydrology of the south basin and outlet stream (Barsch 1969), and the associated glacial coverage from 1850 (www.swisstopo.admin: Glacial Monitoring in Switzerland GLAMOS).

change (Haberkorn et al. 2021). Indeed, long-term monitoring has shown progressive warming (rising air temperatures), increasingly intense precipitation, and accelerating rock-glacier velocities, such as those in the Macun cirque.

Monitoring is an essential component for understanding and projecting environmental change. It provides fundamental information for environmental decision-making, policy development, and guidelines in the management of natural resources. The Alps are the water tower of Europe (Tockner et al. 2009), and thus monitoring of alpine surface waters is imperative for the wellbeing of human populations inhabiting downstream landscapes. Changes in water availability in the Alps have already affected the tourist landscape, with human interventions being continuously necessary to sustain economic stability (Zarrineh et al. 2020). Other changes have occurred with respect to hydropower generation (e.g. increases in small head hydropower facilities, Lange et al. 2018; Crnobrnja-Isailovic et al. 2021), and the ongoing switch to alternative energy sources. Lastly, water-quality monitoring provides baseline environmental information in understanding changes in the ecology of water resources

such as aquatic biodiversity (Jacobsen et al. 2014). Monitoring data are clearly important in understanding changes in aquatic environments in response to the rapid and ongoing changes in alpine landscapes globally (FOEN 2021).

The primary aim of this paper was to summarize long-term physico-chemical data from a high-elevation stream-lake network, the Macun Lakes, in the Swiss National Park, eastern Switzerland. A second objective was to compare the water physico-chemistry of 30 springs and tributaries in the network between 2002 and 2017. A final objective was to examine seasonal and diurnal patterns of specific physico-chemical parameters, which were recorded continuously between 2016 and 2019 using an Exosonde (YSI EXO2) near the outlet of the last lake in the fluvial network in the catchment. The data demonstrate the importance of long-term ecohydrological monitoring of alpine aquatic systems in the context of environmental change. This paper follows up on an earlier paper (Robinson & Oertli 2009), adding to that database and showing that surface waters in Macun are experiencing decreasing influence of (rock-)glacier waters.

Site description

The Macun Lakes region (46° 44' N, 10° 08' E) is a high-alpine cirque (> 2,600 m asl) in the Graubunden Canton, Switzerland (Figure 1). The 3.6 km² region, annexed to the Swiss National Park in 2000, is an area designated for long-term monitoring of Alpine streams and lakes. The drainage network of Macun consists of a north and a south basin (Figure 1). The region comprises 26 small lakes and ~10 small temporary ponds; the four largest lakes, excluding lake Dragun, are interconnected by stream segments, each < 500 m long (Robinson & Oertli 2009). The large lakes cover ca. 0.12 km² each and are < 10 m deep. The surrounding peaks reach elevations of 2,800 to 3,000 m asl, and the outlet stream (Zeznina) drains north to the Inn River near the village of Lavin, Switzerland, in the lower Engadine. The elevations of the study sites were between 2,610 and 2,650 m asl. Water sources in the catchment originate from precipitation (mostly as snow in winter) and seven rock glaciers (Barsch 1969) associated with the south basin. Specifically, inputs from a large rock glacier (Macun1 in Barsch 1969; Fehr & Reich 2015; Derungs & Tischhauser 2017) affect only the surface waters assessed at Zeznina (site 29), although the six other small rock glaciers provide meltwaters to the south-basin stream network (see Figure 1). Recent assessment of the large rock glacier (Macun1) has indicated substantial activity over recent decades (Fehr & Reich 2015; Derungs & Tischhauser 2017).

Precipitation is low, around 850 mm / y⁻¹, and air temperature ranges from 20°C in summer to −25°C in winter (Buffalora meteorological station, ~14 km southeast of Macun). Our newly installed meteorological station at Macun (at site 28 in Figure 1) recorded a maximum temperature of 18.7°C in July 2019 and a minimum of −23.2°C in January 2019. Bedrock geology is slow-weathering crystalline (ortho-gneiss, meta-granitoid) rock (see Figure 1). The area is above the treeline, and terrestrial vegetation is typical alpine grasses and low-lying herbs with areas of bare rock. The area is remote and, being in the national park, is accessible only on foot. Aquatic vegetation is present in some lakes, with Bryophyta (7 taxa) being predominant (Oertli et al. 2008). Helophytes were found in a lower-elevation lake, consisting of *Eleocharis* sp., *Eriophorum scheuzeri, Glyceria* sp., and *Saxifraga stellaris*. No other assessment of the vegetation has so far been made. The large lakes have fish (*Salmo trutta fario, Salvenius namaycush, Phoxinus phoxinus*), and were last stocked in 1993 (P. Rey, personal communication).

In contrast to proglacial streams, glacial flour is essentially non-existent in these streams and turbidity is low. Even so, the annual flow regime differs between basins: the south basin experiences more extreme channel contraction from the freezing of water associated with rock glaciers in autumn (Robinson & Matthaei 2007). The stream network, as a whole, contracts by up to 60% in winter. The water source in each basin also causes differences in water chemistry and in water temperature, being warmer in the north basin than the

Table 1 – Summary of physico-chemical data from spot collections at the end of July, from 2001 to 2019 (n = 19 years), except PP 2001–2011 (n = 11 years) and TP 2012–2019 (n = 8 years). Values expressed are means (*pH is given as median), SD = standard deviation, CV = coefficient of variation, Max = maximum, and Min = minimum, NA = not applicable.

		Conductivity	Turbidity	Temperature	pH*	NO₃-N	DN	PN	PO₄-P	PP	GP	DOC	TIC	POC	SiO₂	Alkalinity
		µs/cm	NTU	°C		µg/l	µg/l	µg/l	µg/l	µg/l	µg P/L	mg/l	mg/l	mg/l	mg/l	mmol/L
North Basin	Mean	6.5	1.9	12.2	6.5	69.1	179.5	102.4	2.0	8.6	10.5	0.9	0.9	1.0	2.2	0.11
	SD	0.9	2.6	3.3	NA	20.3	91.6	55.0	1.3	4.1	6.5	0.5	0.4	0.5	0.6	0.03
	CV	13	134	27	NA	29	51	54	65	47	61	53	48	52	28	30
	Max	9.5	18.2	19.5	8.0	108.0	614.0	231.0	4.9	17.1	44.6	2.5	2.5	2.3	4.0	0.21
	Min	4.9	0.2	3.9	5.3	45.0	100.0	0.1	0.4	2.2	6.7	0.5	0.2	0.0	1.4	0.08
South Basin	Mean	10.3	2.0	9.3	6.4	177.6	260.3	33.8	2.3	3.4	7.0	0.7	0.8	0.3	2.4	0.09
	SD	3.1	2.2	3.2	NA	83.2	108.7	26.0	0.7	2.2	2.9	0.6	0.4	0.2	0.8	0.02
	CV	30	108	35	NA	47	42	77	32	64	42	88	47	71	33	21
	Max	24.0	10.7	14.6	7.7	470.0	520.0	157.0	3.6	9.1	17.2	3.6	1.6	1.0	4.1	0.1
	Min	5.3	0.1	2.1	5.2	53.4	101.0	9.2	1.0	0.7	3.8	0.2	0.2	0.1	1.3	0.1
Immez outlet	Mean	9.6	2.6	10.4	NA	113.1	200.9	50.7	4.5	6.7	6.7	0.8	0.8	0.5	2.3	0.10
	SD	1.5	3.5	2.9	NA	38.2	89.6	20.2	5.8	10.8	1.5	0.4	0.5	0.2	0.7	0.02
	CV	15	132	28	10	34	45	40	131	161	23	52	56	50	31	18
	Max	12.6	12.3	15.4	7.7	184.0	360.0	92.0	13.2	48.1	9.4	1.8	1.5	0.9	3.7	0.13
	Min	6.9	0.3	3.6	5.4	69.0	100.0	14.7	1.3	1.4	4.5	0.3	0.0	0.1	1.4	0.08
Zeznina	Mean	19.8	7.9	7.7	6.5	198.1	302.7	33.9	1.9	6.1	8.9	0.6	1.2	0.4	2.7	0.12
	SD	13.9	7.9	2.5	NA	68.0	100.8	34.6	0.7	3.3	5.3	0.3	0.4	0.2	0.8	0.01
	CV	71	99	32	NA	34	33	102	37	54	59	52	35	49	29	12
	Max	26.5	27.9	12.5	7.3	399.0	470.0	147.0	2.9	13.5	21.6	1.3	2.0	0.7	4.1	0.15
	Min	10.5	0.8	2.8	5.5	124.0	155.0	0.1	1.1	1.6	5.1	0.2	0.5	0.2	1.6	0.11

NO₃-N = nitrate-nitrogen, DN = dissolved nitrogen, PN = particulate nitrogen, PO₄-P = ortho-phosphorus, PP = particulate phosphorus, TP = total phosphorus, DOC = dissolved organic carbon, TIC = total inorganic carbon, POC = particulate organic carbon, and SiO₂ = silicate.

south basin. Stream channels in each basin have low gradients and contain mostly stable cobble substrate.

Methods

The study began in September 2001, followed by annual monitoring in late July (summer period) each year during the study period at 10 primary sites (yellow sites in Figure 1). Of these 10 sites, 4 were in the north basin, 4 in the south basin, and 2 in the outlet stream (Immez outlet and Zeznina). The sites were situated at the inlets and outlets of the prominent lakes in each basin along the drainage network. Meltwater from a large rock glacier enters the outlet stream between Immez outlet (site 28) and Zeznina (site 29); Immez outlet represents the outlet of both basins. In 2002 and 2017, all springs and tributaries feeding the lakes and main channel in each basin were sampled around every 3 weeks during the open-water season (typically late June to mid-October), resulting in 30 different sites being sampled (see Figure 1).

A 0.5 L water sample was collected from each site on each visit for analysis of nitrogen constituents (nitrate: NO_3-N; particulate nitrogen: PN; dissolved nitrogen: DN), phosphorus constituents (orthophosphate: PO_4-P; particulate phosphorus: PP; total phosphorus: TP), dissolved organic carbon (DOC), particulate organic carbon (POC), total inorganic carbon (TIC), silicate (SiO_2) and alkalinity, following methods in Tockner et al. (1997) and Robinson & Matthaei (2007) (see Table 1 for summaries of measured parameters). Micro-nutrients and heavy metals were sampled in 2002 and 2017 during the more extensive sampling campaigns in those years. Aluminium (Al, detection limit < 0.5 µg/L), manganese (Mn, < 0.01 µg/L), iron (Fe, < 0.02 µg/L), cobalt (Co, < 0.1 µg/L), nickel (Ni, < 0.10 µg/L), copper (Cu, < 0.10 µg/L), zinc (Zn, < 0.1 µg/L), molybdenum (Mo, < 0.1 µg/L), cadmium (Cd, < 0.1 µg/L), and lead (Pb, < 0.2 µg/L) were analysed by inductively coupled plasma mass spectrometry (ICP-MS). All (except Al, range 38–71 µg/L) were near or below analytical detection limits during the period of study and are not discussed further in this paper (Robinson & Matthaei 2007; Vogler 2018). Spot measures of temperature and conductivity (WTW LF 323, Germany), turbidity (Cosmos, Züllig AG, Switzerland), and pH (WTW pH 330, Germany) were taken at around midday on each visit, using portable field meters. Lastly, temperature loggers (Hobo tidbits) were installed at 3 main sites to continuously record data on an hourly basis during the study period. These sites included the outlets of each basin (north basin at site 11, south basin at site 15, and Immez outlet at site 28; see Figure 1). Tidbits were exchanged and downloaded each year. However, temperature data are missing from August 2007 to August 2009 at all sites due to dead batteries, and for 2019 at site 15 due to a faulty startup of the logger.

Figure 2 – (Top) The Exosonde, with stainless steel shell and support legs for installation in the lake. The shell and support legs protect the Exosonde from heavy snow/ice and avalanche impact during winter. (Bottom) Instruments set up for recording data from the Exosonde as well as the meteorological station; energy from the solar panel is stored via two batteries in the box. © C. Ebi

In July 2016, an YSI EXO2 Multiparameter Sonde (Exosonde) was installed near the outlet of lake Immez at a depth of ca. 1.5 metres. The lake is ice-covered in winter, but the probe is functional all winter. The probe is connected by cable to a separate data-logging station with an ensured power supply (solar panel, 0.27 m²) and data communication capability. In March 2017, the Exosonde was damaged (compacted by heavy snow on ice) and replaced in July 2017 using a modified external stainless steel shell and support rods for better protection (Figure 2). The Exosonde records hourly, transmitting data via satellite twice per day to the National Park headquarters in Zernez, Switzerland. The data are also downloaded at the Eawag Sensor lab. The sensors embedded in the Exosonde are cleaned (sensors also self-clean during operation) and calibrated in spring and autumn of each year; they are replaced when required. In this paper, we report typical diurnal patterns over 7 days during summer,

autumn and winter 2018, and spring 2019 for continuously recorded data of specific conductance, temperature, dissolved oxygen, turbidity, pH and chlorophyll-a.

Data Analysis

Our previous assessments revealed clear basin differences in water physico-chemistry (Robinson & Matthaei 2007; Robinson & Oertli 2009). Thus we first examined the current long-term dataset by statistically summarizing the measured physico-chemical parameters, comparing the south basin, the north basin, Immez outlet and Zeznina. Summary statistics (in tabular form) included the mean, standard deviation and coefficient of variation. Next, spatial patterns were examined using principal component analysis (PCA) with log(X+1) transformed data. Here, sites were summarized in the PCA scatterplot by basin, Immez outlet and Zeznina averaged across time (years) to better illustrate the variation in physico-chemistry within each area over the study period. Temporal changes in physico-chemistry were then assessed by plotting the PCA scores of each basin, Immez outlet and Zeznina, for axis-1 and axis-2 of the PCA used above, across time (years). Simple regression was used to test for any clear temporal change (increase or decrease) in PCA scores from 2001 to 2019.

The long-term continuous temperature data were plotted to visualize differences among the two basins and Immez outlet over the study period. These data revealed seasonal as well as inter-annual differences in water temperature among the three sites. Temperature data were summarized as mean, median, maximum and minimum water temperatures experienced over the study period, and revealed the number of relatively warm days each year that probably influenced the primary and secondary production of surface waters. The number of relatively warm days each year was estimated starting from the distinct temperature inflexion increase in spring to the inflexion decrease in autumn.

Physico-chemistry measured at all sites that had surface flow (N = 30) in 2002 and 2017 was summarized using principal components analysis (PCA) on log(X+1) transformed data. PCA results were plotted as means and standard errors for each basin (north, south) and year (2002, 2017). All PCAs were conducted using SPSS (vers. 25).

The Exosonde recorded a variety of parameters near the outlet of lake Immez at a depth of ca. 1.5 m. Data were initially summarized by plotting over the period of operational time (2017–2019). This assessment revealed strong seasonality as well as strong diel patterns for the parameters measured. 7-day data patterns typical for each season (spring, summer, autumn, winter) were chosen to best illustrate the observed seasonal dynamics in diel patterns. Selected 7-day periods in spring and autumn were used to show the rapid transition in seasonality (i. e., spring to summer, autumn to winter) of the surface waters of lake Immez; the representative 7-day periods for summer and winter were at mid-summer and mid-winter. These data were summarized as means, standard deviations, coefficients of variation, and maximum and minimum values to further illustrate the seasonal differences and the diel nature of the different parameters during the different seasons.

Table 2 – Summary statistics of the long-term water temperature (°C), recorded hourly and continuously, using Hobo Tidbit data loggers. SD = standard deviation, NA = not applicable. Days refer to the summer growth period, which is the (approximate) period between the inflection date of increase in spring and that of decrease in autumn. See map for locations of sites.

	2002	2004	2005	2006	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019
Immez inlet north (site 11)															
Maximum	18.1	18.0	18.5	23.0	18.0	20.6	20.9	21.7	20.9	23.6	22.0	21.8	20.0	NA	19.7
Minimum	0.6	0.1	0.0	0.1	1.9	0.0	0.1	0.2	0.1	0.3	−0.1	0.0	0.0	NA	0.6
Mean	9.0	7.1	7.1	8.4	8.4	8.0	7.7	8.3	7.5	7.4	7.2	7.8	9.1	NA	8.2
Median	8.9	7.0	7.1	7.8	8.0	7.8	8.2	8.1	7.5	7.4	6.5	8.0	9.2	NA	8.3
SD	3.6	4.4	4.2	4.3	2.9	4.3	4.8	4.6	4.9	3.6	5.2	5.0	4.5	NA	4.4
Days	120	126	145	136	NA	128	163	126	135	130	154	135	127	NA	94
Immez inlet south (site 15)															
Maximum	11.4	12.3	16.4	15.3	18.9	12.8	NA	16.4	19.2	15.5	23.4	15.1	16.6	NA	12.7
Minimum	0.7	0.3	0.2	0.5	0.2	0.5	NA	0.4	0.5	0.0	0.3	0.2	0.4	NA	0.6
Mean	5.1	6.4	6.6	7.3	8.9	6.3	NA	6.6	5.9	2.3	6.6	6.8	8.2	NA	6.8
Median	5.0	7.0	6.9	7.3	9.1	6.4	NA	6.1	5.9	5.9	5.3	7.2	8.6	NA	7.6
SD	2.5	2.8	3.4	3.2	3.5	2.4	NA	4.1	3.5	2.6	4.0	3.5	3.3	NA	2.9
Days	143	120	157	134	NA	NA	NA	NA	135	141	153	134	109	NA	94
Immez outlet (site 28)															
Maximum	14.0	13.6	16.3	17.7	19.2	13.7	17.8	18.2	15.5	14.3	17.1	17.4	15.3	17.5	14.6
Minimum	1.1	0.5	0.3	−0.8	0.8	0.6	0.8	0.8	0.9	0.1	0.5	0.5	0.5	0.7	0.5
Mean	8.7	7.5	6.9	7.8	8.2	6.5	7.6	7.5	7.1	6.4	7.1	7.7	6.3	9.3	7.1
Median	9.2	7.9	7.4	7.9	8.6	6.8	8.2	7.6	6.9	6.7	5.9	7.8	4.8	10.0	7.2
SD	2.6	3.2	3.7	3.7	4.7	3.1	4.3	4.1	4.0	2.7	4.5	3.8	4.1	3.7	3.6
Days	139	118	156	139	NA	NA	165	138	133	131	162	138	NA	140	193

Results

Spatio-temporal patterns in basin physico-chemistry (2001–2019)

Surface waters of the Macun catchment are relatively pristine, reflecting the underlying geology and influence of rock-glacier inputs, which are essentially absent in the north basin but present in the south basin. Because the local geology is predominantly orthogneiss and granite, the electrical conductivity of the waters is low (mean = 6.5 µs / cm in the north basin, 10.3 µs / cm in the south basin) (Table 1). Mean conductivity at Immez lake outlet was 9.6 ms / cm, whereas it increased to 19.8 µs / cm at Zeznina due to the input of rock-glacier water between the two sites. Water turbidity (NTUs) was low (ca. 2.5 NTUs or less), increasing to a mean of 7.9 at Zeznina. The median pH of waters was ca. 6.5–6.6 at all sites, again reflecting the slow-weathering bedrock in the area.

Nitrate (NO_3-N) and dissolved nitrogen (DN) values were higher for the south basin and Zeznina than for the north basin and Immez outlet:
- mean NO_3-N = 177.6 (south basin) and 198.1 µg / L (Zenina)
- mean NO_3-N = 69.1 (north basin) and 113.1 µg / L (Immez outlet)
- mean DN = 260.3 (south basin) and 302.7 µg / L (Zenina)
- mean DN = 179.5 (north basin) and 200.9 µg / L (Immez outlet).
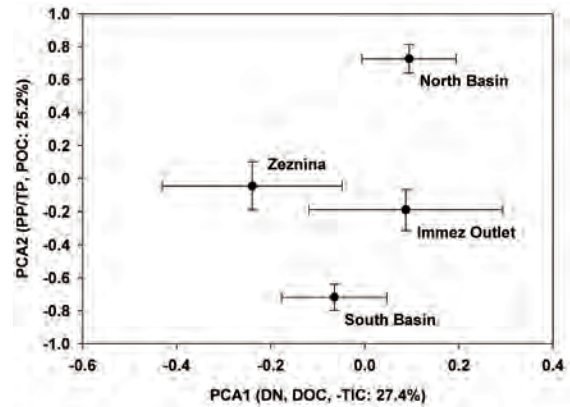
Figure 3 – Scatterplot of the first two axes of a principal components analysis (PCA1, PCA2) using the physico-chemical data collected each year at the end of July. Site loadings are summarized as means and standard errors along each axis for sites located in the North Basin (n = 4), South Basin (n = 4), lake Immez outlet and Zeznina. DN = dissolved nitrogen, DOC = dissolved organic carbon, TIC = total inorganic carbon, PP = particulate phosphorus, TP = total phosphorus, POC = particulate organic carbon.

In contrast, particulate nitrogen (PN) averaged 102.4 µg / L in the north basin but only 33.8 µg / L in the south basin and Zenina (Table 1).

Ortho-phosphorus (PO_4-P) concentrations were similar among surface waters, averaging between 1.9 and 4.5 µg / L (Table 1). In contrast, particulate phos-

*Table 3 – Summary of data for physico-chemical parameters for a representative time period (7 days) in each season in 2018. Parameters were recorded hourly by individual sensors embedded in the Exosonde near the outlet of Lake Immez. See Figure 6 for graphical presentation of the continuous data. Values expressed are means (*pH is given as median), SD = standard deviation, CV = coefficient of variation, Min = minimum, Max = maximum, NA = not applicable.*

| Season		Temperature	Conductivity	Turbidity	Dissolved Oxygen	Chlorophyll-α	pH*
		(°C)	(µS / cm)	(FNU)	(mg / L)	(µg / L)	
Spring	Mean	0.6	5.2	0.68	10.74	−0.02	6.4
30 May–6 June	SD	0.39	0.19	0.08	0.14	0.08	NA
	CV	64.0	3.6	11.8	1.3	327.2	NA
	Min	0.1	4.9	0.53	10.27	−0.19	6.2
	Max	1.5	5.9	0.89	10.89	0.23	6.5
Summer	Mean	13.2	10.4	1.31	8.41	4.80	7.4
7–15 August	SD	0.56	0.30	0.17	0.23	1.65	NA
	CV	4.3	2.9	13.3	2.8	34.4	NA
	Min	11.8	9.9	0.88	7.70	1.21	6.8
	Max	14.9	11.0	1.69	8.94	11.08	8.6
Autumn	Mean	1.7	11.0	1.11	10.24	11.59	6.9
26 October–	SD	0.70	0.36	0.37	0.21	3.60	NA
2 November	CV	41.2	3.3	32.9	2.1	31.0	NA
	Min	0.8	10.5	0.80	9.05	0.92	6.7
	Max	3.8	11.9	5.78	10.54	19.96	7.1
Winter	Mean	0.1	13.6	0.43	7.84	0.08	6.1
19–26 February	SD	0.01	0.36	0.04	0.11	0.08	NA
	CV	14.2	2.7	9.2	1.4	92.1	NA
	Min	0.1	12.9	0.36	7.67	−0.14	6.1
	Max	0.1	14.1	0.89	8.08	0.32	6.1
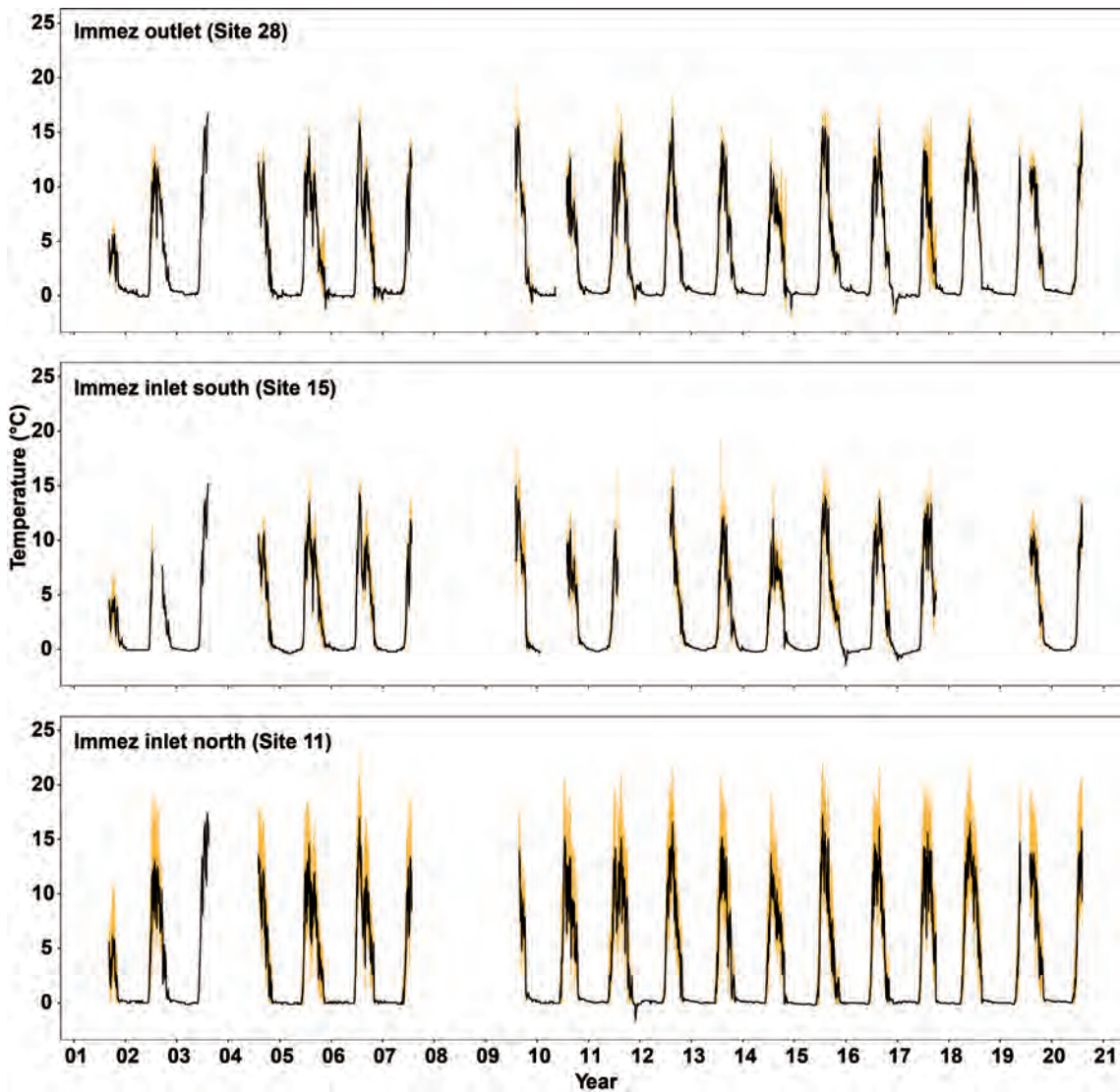
Figure 4 – Long-term temperature (°C) data recorded hourly with data-loggers installed at the north inlet of lake Immez (North Basin network), south inlet of lake Immez (South Basin network), and the outlet of lake Immez. The bold line is the average; the grey line represents minima and maxima. Data is missing from August 2007 to July 2009 because of dead batteries.

phorus (PP) and total phosphorus (TP) were higher in the north basin (8.6 µg/L and 10.5 µg/L, respectively) than in the south basin (3.4 µg/L and 7.0 µg/L, respectively). Further, PP and TP at Zeznina were 6.1 and 8.9 µg/L, respectively; phosphorus values at Immez lake outlet fell between the values of the two basins.

Mean dissolved organic carbon (DOC) and total inorganic carbon (TIC) values were relatively low, averaging 0.65–0.95 m/L for DOC and 0.80–1.21 m/L for TIC. Particulate organic carbon (POC) was generally low, but was higher in the north basin (mean = 0.96 m/L) than in the other sites (mean = 0.34–0.52 m/L). Silicate, a typical indicator of glacial waters, was similar among waters, averaging 2.2–2.7 m/L; mean alkalinity ranged from 0.09 to 0.12 mmol/L (Table 1).

Results from the PCA summarizing the physico-chemical data collected during the 19-year study pe-riod clearly separated sites in the north and south basins of the Macun catchment (Figure 3). PCA axis-1 explained 27.4% of the variation among sites and was loaded most highly by measures of dissolved nitrogen (DN), dissolved organic carbon (DOC) and total inorganic carbon (TIC). PCA axis-2 explained 25.2% of the variation among groups and was loaded highest with measures of particulate phosphorus (PP), total phosphorus (TP) and particulate organic carbon (POC). The data from Immez lake outlet fell mid-way between the basin groups along both PCA axes in the scatterplot. The Zeznina site downstream of Immez outlet, fed by meltwaters from a large rock-glacier, was located the farthest left on axis-1, clearly showing the influence of rock-glacier inputs on its physico-chemistry. PCA axis-2 showed north-basin sites having higher values of PP, TP and POC than south-basin sites, with the values for Immez lake outlet and Zeznina somewhere between those for the two basins.
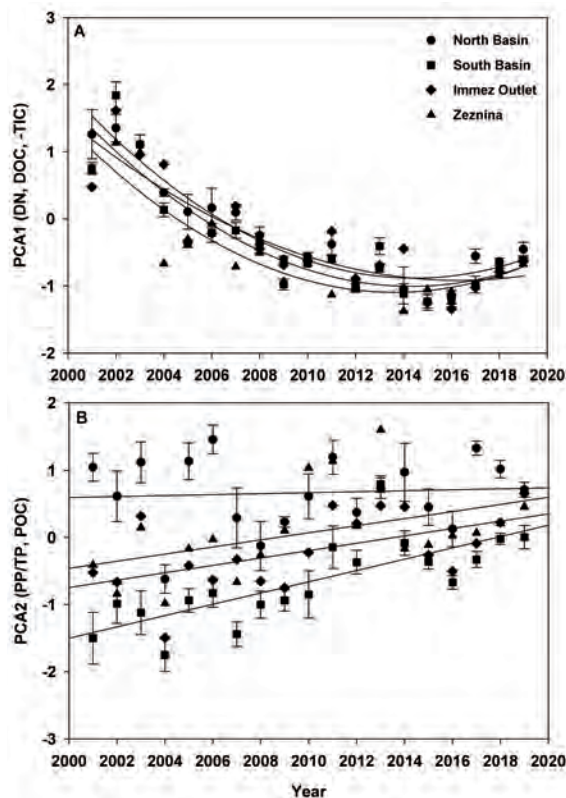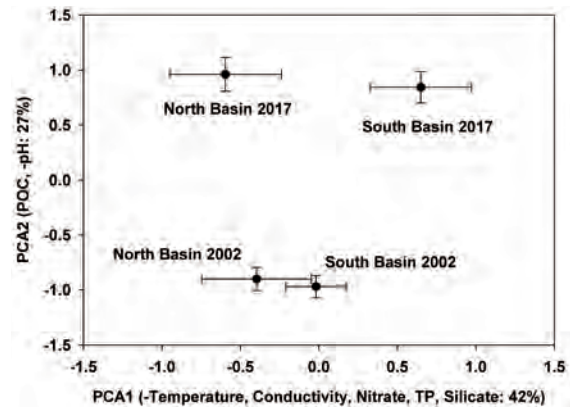
Figure 6 – Scatterplot of the first two axes of a principal components analysis (PCA1, PCA2) using the physico-chemical data collected at spring sites in the North Basin and South Basin in 2002 and 2017. Site loadings are summarized as means and standard errors along each axis for sites located in the North Basin (n = 7) and South Basin (n = 10). TP = total phosphorus, POC = particulate organic carbon.

Figure 5 – Long-term trend lines (regression lines) in physico-chemical parameters that best explained PCA1 and PCA2 of the scatterplot shown in Figure 3. Plots represent temporal changes in North Basin sites (n = 4), South Basin sites (n = 4), lake Immez outlet and Zeznina, from 2001 to 2019. DN = dissolved nitrogen, DOC = dissolved organic carbon, TIC = total inorganic carbon, PP = particulate phosphorus, TP = total phosphorus, POC = particulate organic carbon.

Another evident pattern in the PCA scatterplot was the much higher spread in the data loading axis-1 than in the data loading axis-2.

Continuous long-term records at the outlet of each basin and Immez lake outlet revealed inter-annual differences in temperature patterns but no overall increase or decrease from 2001 to 2019 (Figure 4). Basins clearly differed in temperature: in summer, the north basin always had higher values (most years above 20°C, mean = 12.2°C) than the south basin (less than 20°C, mean = 9.3°C) (Table 1). Immez outlet temperatures were somewhere between those of the two basins or cooler, depending on the year (mean = 9.1°C), reflecting the general contribution and mixing of waters from each basin. In winter, waters in each basin and Immez outlet decreased to near 0°C, and possibly even froze at the recorded sites. The number of days per year with relatively warm waters (> 1.0°C) differed among basins and the outlet, ranging from 120 days (ca. 4 months) to a maximum of 165 days (ca. 5–6 months) (Table 2).

Long-term patterns in physico-chemistry were illustrated by plotting the PCA scores of axis-1 and axis-2 over time (Figure 5). PCA axis-1 showed a decrease from 2001 to 2009, then a general flattening in the data from 2009 to 2019 (albeit a slight increase occurred in 2019). These data indicate a general decrease in DN and DOC, and an increase in TIC, from 2001 to 2009, with little change in values from 2009 to 2019. In contrast, data from PCA axis-2 showed a general increase in PP, TP and POC over the study period for south-basin sites, Immez lake outlet and Zeznina. North-basin sites remained relatively unchanged in PCA axis-2 scores during the study period and, as mentioned above, had the highest PCA axis-2 scores among groups. Of note is that the variation among data loading on PCA axis-2 decreased from 2001 to 2019 (the variation was less on PCA axis-2 than for PCA axis-1 scores), suggesting a temporal homogenization in the physico-chemistry of waters in the Macun catchment overall (Figure 5).

Long-term physico-chemistry of springs and tributaries (2002 versus 2017)

PCA based on the physico-chemistry of springs and tributaries in the Macun catchment (see Figure 1, map) revealed differences between basins and between years (here, 2002 versus 2017) (Figure 6). PCA axis-1 explained 42% of the variation among sites and was loaded with measures of temperature, conductivity, nitrate, TP and silicate. PCA axis-2 explained an additional 27% of the variation among sites and was loaded with POC and pH. PCA axis-1 best represented the differences observed between the north-basin springs and the tributaries lying left of those from the south basin. PCA axis-2 best represented the temporal differences between 2002 and 2017 within each basin, with 2002 being lower on the plot than 2017 (Figure 6). The patterns shown in the PCA support the differences between basins evident in the physico-chemistry of the main channel sites as well as the tem-
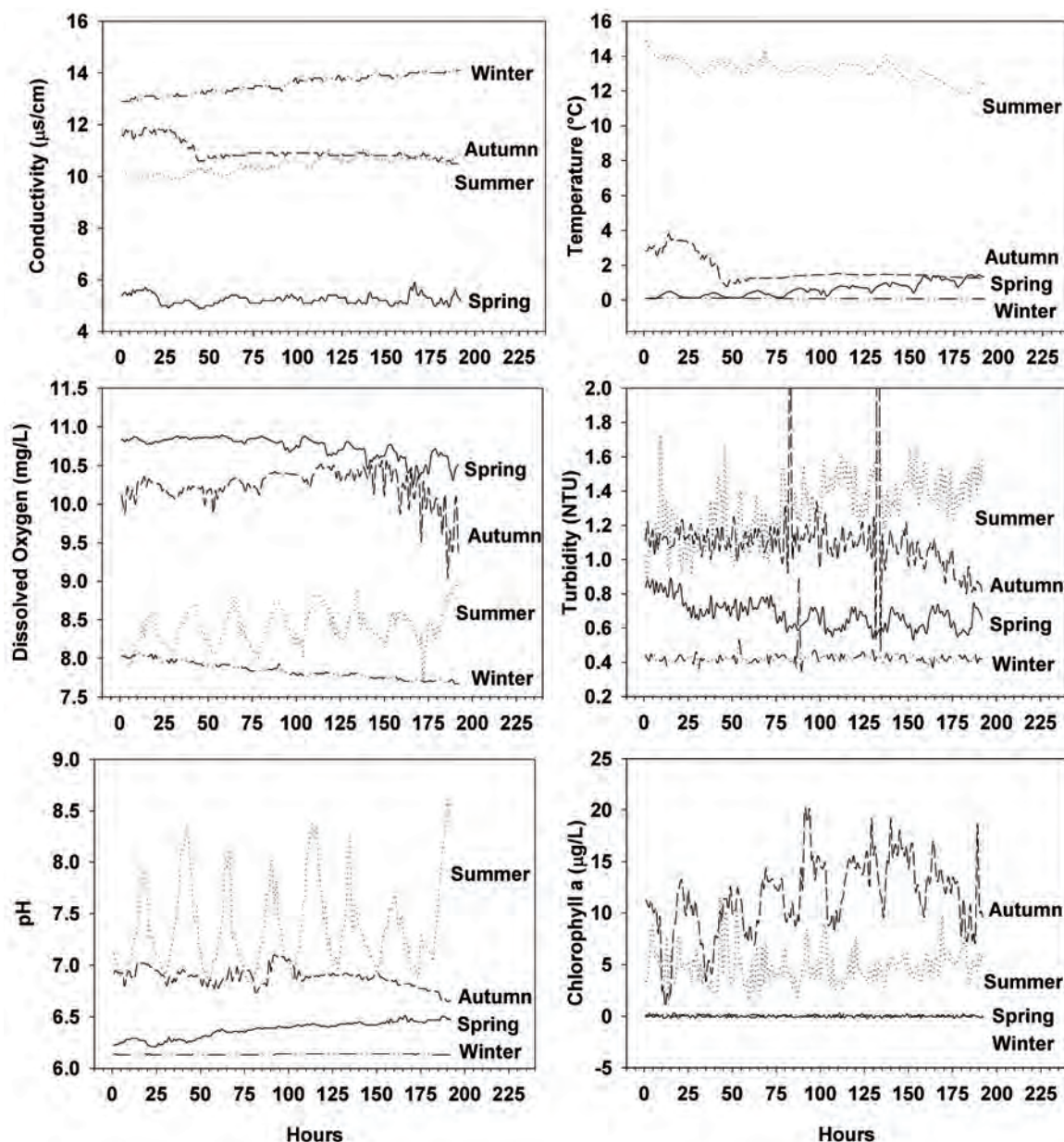
Figure 7 – Plots of continuously recorded (hourly) physico-chemical variables from individual sensors embedded in the Exosonde located near the outlet of lake Immez. Plots show a representative time period (7 days, as noted in Table 3) for each season in 2018.

poral changes in some physico-chemical parameters in the catchment overall.

Seasonal and diel physico-chemistry at the basin outlet in 2018

The Exosonde near the outlet of lake Immez continuously recorded data for conductivity, temperature, dissolved oxygen, turbidity, pH and chlorophyll-a. Typical patterns of one selected week in each season are shown in Figure 7. Conductivity values in general were low in Macun (<16 µs/cm), where maximum values were observed in winter (12–14 µs/cm) and minimum values in spring (<6 µs/cm) (Table 2). Some minor diel variation in conductivity was evident in spring and summer, with higher values during the day than night. Maximal temperatures were observed

in summer (14–16°C) and minimal temperatures in winter (near 0°C) (Table 3). Maximum temperatures in spring and autumn ranged from 2 to 4°C. Diel variation in temperature was notable in spring and summer, when temperatures were warmer during the day than at night (Figure 7). Dissolved oxygen concentrations were highest in spring and autumn (10–11 mg/L), and lowest in winter (ca. 8 mg/L). Strong diel variation in DO was present in summer (ca. 1 mg/L change between day and night), being maximal during the day. In general, the summary of data in spring showed the transition from essentially no diel variation in winter to relatively strong diel curves in summer. In contrast, the summary of data in autumn depicted the rapid decrease in diel variation as winter became dominant in the catchment (Figure 7).

Water clarity, shown as turbidity, was low, but also showed strong seasonality, being highest in summer (ca. 1.3 NTUs) and lowest in winter (ca. 0.4 NTUs) (Figure 7, Table 3). The data summary also revealed some peaks in turbidity associated with local rainstorms; diel patterns were visible in spring. The seasonal patterns in pH showed the lowest values in winter (ca. pH 6.1); values were highest in summer, when strong diel patterns were evident (pH value minima ca. 7.0; maxima 8.0–8.5) (Table 3). Water chlorophyll-a values (sonde accuracy was 0.01 µg/L) were minimal in winter and spring (close to 0 µg/L), intermediate in summer (ca. 4.8 µg/L), and maximal in autumn (11.6 µg/L) (Table 3). The autumn values showed the greatest diel variation (from ca. 1.0 µg/L during the night to a maximum of 19.9 µg/L during the day) (Figure 7).

Discussion

The Macun Lakes are in an alpine cirque. They encompass a variety of water sources, from groundwater springs to rock glaciers, and drain into two separate basins. Various lakes along the main outflow channels are interconnected. The Macun Lakes area also comprises a number of intermittent ponds and small tributaries. As such, it represents an excellent area for the long-term monitoring of the effects of environmental change on alpine waters. The results clearly showed between-basin differences as well as temporal changes in the physico-chemistry of surface waters during the 19 years of monitoring. The assessment of springs and tributaries between 2002 and 2017 reflected the spatio-temporal changes observed in the main-channel study sites. Lastly, Exosonde data revealed strong diel and seasonal shifts in the physico-chemistry of surface waters, emphasizing the active functional role of lakes in alpine fluvial networks.

Rock-glacier input is the primary explanation for physico-chemical differences between the north basin (no rock glacier) and south basin (presence of rock glaciers). In fact, the south basin lies mostly over moraine deposits, and rock glaciers are still active contributors of water to the system (Robinson & Oertli 2009). In contrast, the north basin lies mostly over local bedrock and relatively thin soils, and glacial-water inputs are minimal or absent. A glacial-water signature, or lack of, is clearly visible in the colour of lake water (even with the low turbidity values): the colour is more greyish-blue in the south, while the lake waters in the north basin are browner (authors' personal observation). A glacial-water signature is also seen in physico-chemistry differences between the basins. For instance, in the north basin particulate forms of nitrogen and phosphorus were ca. 2–3x higher than in the south basin, and water temperature in the south basin was ca. 3°C lower (see also Robinson & Matthaei 2007). One possible explanation for the differences is that rock glaciers are typically associated with perma-

frost areas. Climate warming may have increased the amounts of solutes from permafrost/rock glacier in the surface waters of the south basin. Further, these relatively small rock glaciers in the south basin may be more sensitive to precipitation events than larger rock glaciers. As the basins lie over gneiss and granitic bedrock, ion concentrations of the waters in both basins were generally low, with mean electrical conductivities typically being below 10 µs/cm.

The physico-chemistry of the catchment changed over the study period. Around 2007, dissolved nitrogen in the catchment was lower than in 2001 (Robinson & Oertli 2009), and decreased further between 2007 and 2019 (see Figure 5). The pH of waters in both basins also increased, from < 6.0 in the late 1970s (Schanz 1984) to 6.5–7.0. Over time, other parameters, such as PP and POC, have changed more in the south basin than in the north basin, probably reflecting the general decrease in rock-glacier inputs in the south basin. Importantly, over the study period, the changes in physico-chemistry of the south basin have shifted the basin's chemical signature closer to that of the north basin. This change suggests that the physico-chemistry of surface waters in the catchment are becoming more similar over time. As both basins lie over similar geology, the ongoing reduction in rock-glacial waters will continue the process of homogenization. The question remains as to how long a glacial legacy effect will be present in south-basin waters (a glacial legacy has been observed in other alpine streams in the area, see Sertic Peric et al. 2015).

The springs and tributaries monitored in 2002 and 2017 also revealed temporal changes in both basins, while the basin-level differences observed at main-channel sites remained. The temporal changes revealed in the PCA were subtle differences in pH (lower in 2017) and POC (higher in 2017); basin-level differences were for the same variables as in the main dataset. It is important to note that most tributaries (ca. 70%) are precipitation-fed and intermittent, typically drying up in late summer (Robinson & Matthaei 2007), as also documented in the nearby catchment Val Roseg (Paillex et al. 2020).

The records for temperature, which was logged hourly at the outlets of each basin and in the outlet of the catchment, clearly demonstrate the sensitivity of alpine surface waters to local climate conditions. The area is relatively small. Thus, differences in solar radiation exposure between the basins are minimal. The warming of alpine waters under climate change has been documented (Webb & Nobilis 2007), but our data also show that inter-annual differences in weather play a significant role in dictating surface-water temperatures in the Macun catchment. For instance, although a 3°C difference occurred between basins (due to the rock-glacial water inputs in the south basin), strong inter-annual differences were observed over the study period and in both basins. Maximum temperatures between 2002 and 2019 ranged from 18.0

to 23.6°C in the north basin, from 11.4 to 23.4°C in the south basin, and from 13.7 to 19.2°C at the catchment outlet at Immez; no general warming trend was observed over the study period (at 19 years long, however, it was relatively short for the detection of trends) (see Table 2). Although streams are fairly shallow, slow-flowing and interconnected by small lakes, the high maximum temperatures in some years (> 23°C) is alarming. The network of lakes and streams increases water residence times and further enhances the potential for heating via intense solar radiation, even though rock-glacial inputs maintain cooler waters in the south basin (e.g. Lissi et al. 2015). Piccolroaz et al. (2018) showed that the temperatures of glacial-fed streams during heatwaves may be buffered by glacial water inputs that keep the waters cool. For Macun, this finding suggests that north-basin streams lacking glacial inputs are probably more sensitive to solar heating than south-basin streams, and will continue to be so until rock-glacial inputs diminish, as is expected to happen in the near future (see e.g. Woodward et al. 2016).

Sensor development has enhanced the potential for continuous remote monitoring. The Exosonde used in the present study recorded data, for a number of physico-chemical parameters, which were downloaded via satellite twice a day and displayed in real time at the Swiss National Park visitor centre (www.nationalpark.ch). The unit is solar-powered (with backup batteries), and was recently coupled to a meteorological station. The Exosonde was placed near the outlet of the last lake in the network, at 2,600 m asl. The data clearly demonstrated both strong seasonal patterns and diel dynamics for recorded variables (see Figure 7).

Values for conductivity, temperature, turbidity and pH displayed extremes between summer and winter; temperature, turbidity and pH were maximal in summer, and conductivity was maximal in winter (see Figure 7). In contrast, dissolved oxygen was maximal in spring and autumn; chlorophyll-a was maximal in autumn and intermediate in summer. These seasonal patterns reflect the ecosystem processes and functioning of the alpine waters during the annual cycle. Little or virtually no activity was evident in winter, as the system is completely snow-covered and water inputs come solely from groundwater. Spring activity reflects renewed biological functioning of the waters and benthic processes; summer and autumn reveal seasonality in ecosystem production (e.g., phytoplankton and benthic biofilms) and respiration (decomposition of benthic organic matter). Dissolved oxygen levels were lower in summer than in spring and autumn, probably due to the increased microbial activity (respiration) in the decomposing organic matter accumulated during winter. Interestingly, such patterns were similar to those of an earlier study assessing the ecosystem metabolism of Macun's streams: this study found that respiration was higher in early summer than in the autumn, due to the metabolic processing of accumulated organic matter by microbes (Logue et al. 2004).

The diel data from the Exosonde indicated how rapidly ecosystem processes start up in spring and slow down in autumn. For example, strong diel patterns in dissolved oxygen became evident during the week of recording in spring, whereas a breakdown of the DO diel pattern was evident in the 7-day record for the autumn (see Figure 7). A diel pattern was also evident for temperature in spring and summer; no diel temperature pattern was evident in the autumn or winter data. The chlorophyll-a data showed a strong diel pattern in the autumn, and a weaker one in summer. These data suggest seasonal changes in phytoplankton dynamics in alpine waters, and in lakes in particular. One explanation for the difference between summer and autumn could be changes in grazing activity by zooplankton (which is greater in summer than in autumn); this needs to be examined further. The diel phytoplankton variation in summer, when changes in dissolved oxygen reached almost 1.0 m / L between day and night, was also reflected in the large diel curves in pH (a difference of almost one pH unit between day and night). Although the data shown are for a typical week of any given season, long-term continuous monitoring will provide even greater insights into how alpine surface water functions in relation to environmental change. The coupling of other sensors (e.g., biotic) with physico-chemical sensors is recommended for future studies and monitoring networks.

To summarize, long-term monitoring helps to predict future environmental changes in ecosystem properties (here, those of alpine surface waters). These data, in turn, assist resource managers in environmental decision-making. Long-term data also provide important information towards understanding the drivers of environmental change, and the triggers for ecosystem state changes at tipping points. In particular, long-term data allow us to identify and focus on those parameters that are critical in comparative studies, and to avoid having to run the full suite of measures recorded in this study. Further, the development of new sensors will add to the toolbox of monitoring possibilities, and could enhance our mechanistic understanding of environmental change as well, especially when different types of sensors (e.g., abiotic and biotic) are evaluated together.

The physico-chemistry data from Macun show the sensitivity of alpine waters to environmental change, as well as to annual differences in weather. An important finding was the overall homogenization of surface waters as glacial inputs have diminished over time – a process that is likely to be a response of many glaciated alpine catchments globally. Lastly, the Exosonde data from the last lake in the fluvial network also revealed the strong metabolic patterns at seasonal and diel scales. The combination of lakes and streams in alpine landscapes should be considered in future surface-water monitoring programmes.

Acknowledgments

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