

MASTER PROJECT

The role of glaciers as sources of stream nutrients in a high mountain catchment

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Abstract

In the high mountain environments, streams often appear nutrient-limited. In glaciated catchments however, glacier meltwater acts as sources of nitrogen (N) and phosphorus (P) to downstream ecosystems, but research investigating the spatio-temporal control that mountain glaciers are exerting on stream nutrient dynamics are rare, particularly in the Alps. In this study, we rely on a synoptic spatially distributed sampling of the main glacier-fed stream and major tributaries in a Swiss catchment. By applying a mixing model to estimate glacier meltwater fractions at different locations of the fluvial network, we correlate glacier meltwater contribution with stream nutrient concentrations to depict the glacier control. Moreover, we show that glaciers not only release high quantities of nitrate but also modify the relative abundance of N-species. Finally, we assess phosphate, ammonium and nitrate loads from glacier-fed and groundwater-fed streams to highlight the importance and diversity of glaciers as sources of streamwater nutrients at catchment scale.

Les conditions difficiles des hautes montagnes limites souvent les cours d'eau en nutriments. Cependant, dans les bassins versants glaciaires, la fonte des glaciers agit comme sources d'azote (N) et de phosphore (P) pour les écosystèmes en aval. Toutefois, les recherches sur le contrôle spatio-temporel que les glaciers exercent sur la dynamique des nutriments dissouts sont rares, en particulier dans les Alpes. Dans cette étude, nous nous appuyons sur un échantillonnage synoptique spatialement distribué du torrent glaciaire principal et de ses affluents majeurs dans un bassin versant suisse. En appliquant un modèle de mélange afin d'estimer les fractions d'eau d'origine glaciaire dans nos échantillons, nous établissons ensuite une corrélation entre ces fractions et les concentrations en nutriments dissouts afin de décrire le contrôle exercé par les glaciers. De plus, nous montrons que les glaciers non seulement libèrent de grandes quantités de nitrate mais modifient également l'abondance relative des espèces d'azote. Enfin, nous évaluons les flux en phosphate, ammonium et nitrate dans les cours d'eau glaciaires et nous les comparons à ceux des cours d'eau principalement alimentés en eaux souterraines. Ceci nous permet de souligner l'importance et la diversité des glaciers en tant que sources de nutriments dissouts à l'échelle du bassin versant.

Keywords: *High mountain streams, alpine, glacier, nutrients, mixing model*

1 Introduction

Nitrogen (N) is the major element of Earth's atmosphere and the fourth most abundant element in cellular biomass. This element is required for plant, microbial and animal growth and together with phosphorus (P) they represent key limiting nutrients for most aquatic and terrestrial ecosystems (Conley et al. 2009). At cellular scales, P is required for DNA and RNA synthesis as well as for energy transfer while N is important for protein formation (Conley et al. 2009). N is also known to play a key role in carbon sequestration by favoring carbon accumulation in the biosphere, particularly through biological fixation by microorganisms (Hungate et al. 2003). These processes play important roles in the sensitive climate equilibrium and are thus of primary importance in times of climate change.

Streams and rivers continuously interact with the terrestrial environment along the lateral, longitudinal and vertical dimensions. Moreover, on the temporal scale, the changes in these interactions cause lotic ecosystems to evolve in continuous dynamics (Ward 1989). Headwater streams act as sources of water and nutrients to large rivers and despite their relatively small discharges their controlling role on nutrient export is of great importance for downstream ecosystems (Peterson et al. 2001). Whereas N and P are essential for the development of plant, animal and bacterial life, an overabundance of these nutrients may lead to algal blooms and consequent lack of dissolved oxygen for the aquatic ecosystems (Conley et al. 2009).

High mountain streams often appear resource limited in terms of nutrients (Robinson and Gessner 2000) which are heterogeneously stored in poorly developed soils, snow, permafrost and ice. Among other processes, melting of cryospheric reservoirs controls the mobilization and export of solutes to receiving streams. In glaciated catchments, glaciers play an important role in dissolved carbon and nutrient dynamics as they can act as sources of carbon, nitrogen and phosphorus via different pathways (Brighenti et al. 2019; Hood et al. 2015; Milner et al. 2017). While atmospheric

deposition plays an important role in the release of N to glacier meltwater (Colombo et al. 2019), the effect of microbial communities mediating chemical reactions in the glacial ecosystems can also be important (Hodson et al. 2008). Geochemical weathering at the glacier base (Tranter et al. 2002) constitutes another mechanism by which glaciers influence the streamwater chemistry of downstream reaches. Moreover, physical erosion of bedrock may lead to N and P release and is likely to be an important factor in the dynamics of post-glacial ecosystems (Hodson 2006; Houlton, Morford, and Dahlgren 2018). While such weathering of P has been known for long, rock weathering of N remains a less explored pathway. Indeed, rocks may act as a direct and underrated source of N due to high N content within the rocks themselves and high erosive power present in the high mountain ranges of the world. High erosive power in these regions is a consequence of reduced soil coverage and the presence of strong weathering processes (Houlton, Morford, and Dahlgren 2018). Glaciers may well act as one of these erosive forces as their weathering power shaping the landscape is well established (Hallet, Hunter, and Bogen 1996; Koppes 2020). Due to differences in underlying bedrock and heterogeneous patterns in atmospheric N deposition as well as to the difficulty to assess the contribution of microbially mediated processes within glaciers, the precise way by which glaciers control downstream nutrient concentrations is still unclear although their importance in this context is undebated (Brighenti et al. 2019; Colombo et al. 2019; Milner et al. 2017; Tockner et al. 2002).

While past research has explored how catchment processes regulate the export of carbon and nitrogen to high mountain streams mostly on a seasonal time scale, important gaps in our understanding remain. Most notably, studies to date have primarily focused on seasonal patterns, but the influence of glaciers on fine-scale spatio-temporal dynamics has not been assessed. Moreover, research investigating the importance of glaciers on headwater nutrient patterns are also rare (Colombo et al. 2019; Tockner et al. 2002) since

most studies have focussed on dynamics of dissolved organic and inorganic carbon species (Canadell et al. 2019; Singer et al. 2012). Finally, studies have focused on the dynamics and supply of individual nutrient species, but efforts to assess the balance or proportions of different nutrient forms (e.g., comparing ammonium to nitrate) delivered across alpine catchment patches remain rare (Colombo et al. 2019; Tockner et al. 2002). In the context of rapidly shrinking glaciers (Gardner et al. 2013) and consequent alterations of the hydrological and biogeochemical regime of glacier fed headwater streams (Brighenti et al. 2019; Milner et al. 2017), elucidating these knowledge gaps about the role of glaciers controlling downstream nutrient dynamics is of key importance.

This study aims at examining whether glaciers exert a dominant spatio-temporal control on stream nutrient patterns. In order to better understand the role of glaciers as sources of N and P species and their downstream patterns and fate, a synoptic sampling was performed at the beginning of September 2020 in a partially glacierized catchment in the Swiss Alps. As the glacial influence on the downstream fluvial network is the focus of this research, the sampling was carried out both during morning (expected minimum glacial influence) and afternoon periods (expected maximum glacial influence). In the course of this sampling, 21 points along the main glacier fed stream were sampled along with 10 major tributaries, thus covering an altitudinal gradient of 800 m. An end-member mixing analysis was applied to the reduced space of a principle component analysis to estimate the contribution of glacier melt and groundwater to each sample. The glacier control on streamwater nutrient concentrations was assessed by correlating the resulting fractions of glacier meltwater with the nutrient concentrations, and by assessing the potential relation with the NH_4/NO_3 ratio. The spatial extent of the glacier control on stream nutrient dynamics was estimated by analysing longitudinal differences between morning and afternoon nutrient patterns. Finally, the role of the catchment as a source or sink of nutrient species was assessed by comparing outlet

nutrient loads with source inputs to the main stream.

2 Materials and methods

2.1 Site description

The Valsorey catchment in the Swiss Alps, canton of Valais ($7^{\circ}14'47''$ E, $45^{\circ}55'32''$ N; Figure 1) spans over an area of 25.1 km². The catchment elevation ranges from 1850 m.a.s.l to 4300 m.a.s.l. Three glaciers (Gl. de Valsorey, Gl. du Sonadon and Gl. du Tseudet; Figure 1) are present in the highest parts of the catchment. Streams flowing from the Valsorey and Sonadon glaciers join at a major glacial floodplain located around 2400 m.a.s.l to form the main stream of the catchment - the Torrent du Valsorey. Further downstream, the valley geomorphology constrains the main stream into a canyon-like channel after having received the stream flowing from the Tseudet glacier as well as two tributaries. When the channel walls gradually open up again, the main stream separates into different branches as it crosses

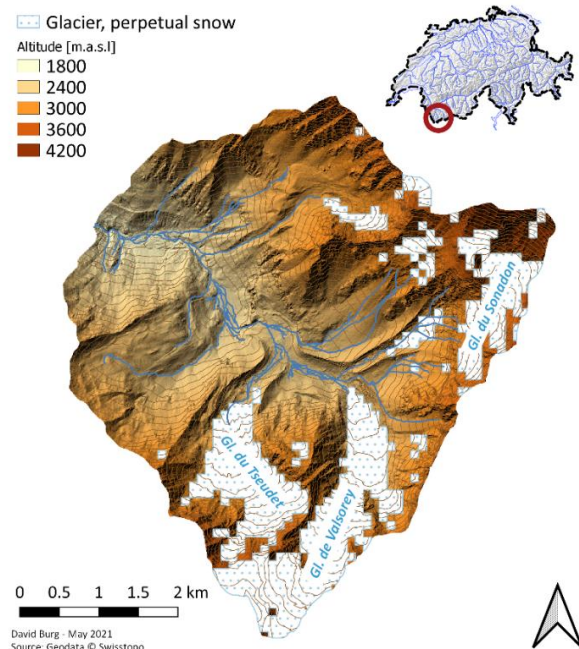


Figure 1: The Valsorey catchment with its three glaciers, main stream and major tributaries, surrounded by steep slopes at an altitude mostly above 2000 m.a.s.l. Glacier extent is based on the Swiss Land Cover statistics (Bodenbedeckung 2019)

a flatter section and joins with more tributaries. From about 2100 m.a.s.l to the outlet, the stream grows as more tributaries join and the flow velocity increases as a steeper section is crossed, ending up in a narrow canyon close to the outlet. Beyond the limits of the study areas, the Torrent du Valsorey first flows into the Dranse d'Entremont to finally join the Rhone river. From the Valsorey glacier to the outlet of the catchment, the Torrent du Valsorey has a length of about 5 km and counts a Strahler order of 4 at the outlet. From the highest regions to the outlet marked by a small dam from which water is diverted into a bigger hydropower plant, the catchment has remained very natural as there are no driving roads and little human impact except for extensive cow farming in the lower areas of the catchment. Bedrock in Valsorey consists of a mixture of crystalline rocks (mainly gneiss and some schist) and unconsolidated sedimentary rocks (postglacial moraine). According to the Swiss landcover assessment, the land cover in Valsorey is comprised of solid rock and rocky areas (36 %), granular soil (25 %), glaciers and perpetual snow (21 %), grass and herb vegetation (9 %), brush meadows and shrubs (7 %) as well as an area of brush forest (2 %) on the left bank of the lower catchment areas (Bundesamt für Statistik (BFS), GEOSTAT 2019). The Valsorey catchment is part of the Metalp monitoring program, where research on catchment hydrology and biogeochemistry has been ongoing since 2016 (see <https://metalp.epfl.ch/> for a full description of the study area, current projects, past publications and data portal”).

2.2 Sampling design

To obtain the most complete picture of the nutrient fluxes within the drainage system, the main glacier-fed stream as well as all major tributaries flowing into it were sampled (Figure S1). At each site, 4 sampling points were typically defined: The upstream (U) served as a local reference while the downstream (D) point measured immediate effects due to the inflow of the tributary (T) which was also sampled. The downstream plus (Dp) was located approximately 50 m downstream of the confluence and was designed to show potential

effects originating in the mixing of the two streams. Naturally, this scheme had to be adapted due to topographical constraints or to allow for a more efficient sampling. In the final sampling design sites 2, 3, 4, 5 and 9 followed this fundamental approach while sampling at sites 1, 6, 7, 8, 11 and 12 was adapted. The main goal remained to obtain a complete picture of all the major streams within the Valsorey catchment.

The field sampling campaign was carried out in 2020 on September 3rd and 4th, which according to data from previous years, corresponded to the end of the season of maximum glacier ablation (Figure S3). Therefore, the glacier's influence on the stream dynamics was expected to still be dominant. To capture the potential effects from diurnal fluctuations in streamwater dissolved nutrients owing to glacier ice melt, the spatial sampling described above was carried out twice. Once in the morning (M) when the influence of glacial meltwater in the main channel was expected to be small, and once in the afternoon (A) when the glaciers melt, and their impact therefore would be high. These sampling windows were chosen based on high-frequency observations of discharge at the existing Metalp monitoring stations (Figure S3). The increasing limb during early afternoon was expected to indicate the addition of glacial meltwater to the stream. Therefore the "Afternoon" campaign was performed on September 3rd from 13:00 to 20:00 and the "Morning" was operated the next day from 7:00 to 13:00. In addition, three water autosamplers (ISCO, USA) were placed at contrasted streams in the catchment aiming to capture the diel cycle of dissolved nutrients in a finer resolution than only morning and afternoon. The first autosampler was placed just downstream of the snout of the Valsorey glacier while the second one was set up a few meters upstream of the catchment outlet. The third ISCO was placed at the tributary 6T. All three autosamplers were programmed to take a water sample every hour starting at 6 AM and going on for one full 24h cycle.

2.3 Physicochemical and hydrological determinations

At each sampling point, parameters such as streamwater temperature, pH, electrical conductivity, and dissolved oxygen were measured using WTW portable multi-parameter probes (Xylem Analytics, USA). To consider the DO data in a form that is corrected for the influence of temperature, the percentage of saturation was used. Similarly, turbidity was measured in-situ using either Cyclops-7 sensors (PME, USA) or a WTW multi-parameter probe (Xylem Analytics, USA). The sensors were kept in the streams for around 10 minutes and the average of the recorded values was used in an intercalibration between the sensors after the field visit. In addition, streamwater samples for the analysis of dissolved organic carbon (DOC) and water isotopes ($\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and $\delta^2\text{H}$) were taken. The samples were filtered using double precombusted GF/F filters (Whatman, USA) and acid-washed, precombusted glass vials. The samples for isotopes were analysed in the following days using a Picarro L1102i wavelength-scanned cavity ring down spectroscopy system (Picarro Inc., USA). The samples for DOC were analysed in the following days using a Sievers M5310c TOC Analyzer (GE Analytical Instruments, UK). Samples for streamwater nutrients (PO_4 , NH_4 , NO_2 , NO_3) were first filtered using double precombusted GF/F filters (Whatman, USA). The samples were then transferred into acid-washed, precombusted glass vials and analysed with a Lachat QuikChem 8500 Flow Injection Analyzer (Hach, USA) applying the following methods for the respective nutrients: 10-115-01-1-M (PO_4), 10-107-04-1-B (NO_3/NO_2), 10-107-05-1-C (NO_2) and 10-107-06-3-D (NH_4). Since NO_2 concentrations were mostly below detection limits (5 ppb) and NO_3 values were orders of magnitude larger, NO_x was considered to represent NO_3 concentrations.

Finally, the stream discharge was measured in each sampled tributary and at 7 locations in the main channel (Figure S1). Discharge was determined using slug injections of sodium chloride (NaCl) as a conservative tracer (Gordon et al. 2004). Therefore, a known

quantity of salt (NaCl) was diluted in water. The mixture was then released close to the middle of the stream at a distance of 30 to 50 m upstream depending on stream size. The increase in conductivity due the salt dilution travelling downstream was measured using conductivity probes (Xylem Analytics, USA) and the resulting conductivity time series were integrated to compute the stream discharge.

2.4 Data analysis

2.4.1 Water source apportionment

A two-end member mixing model based on the major axis of a principle component analysis (PCA) was used to estimate the fraction of glacier meltwater in each sample. The applied method was adapted from the work by N. Christophersen and R. Hooper (Christophersen and Hooper 1992; Hooper 2003; Hooper, Christophersen, and Peters 1990). The sites were first displayed in the reduced space of a PCA based on conservative tracers including ions (sodium, chloride, sulfate, calcium, magnesium, and strontium) and water isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$), as well as streamwater turbidity and temperature.

Under the assumption that stream water primarily derived from a mixture of groundwater and glacier meltwater, the first PCA axis was chosen as the basis for the mixing model. In classical end member mixing analysis, samples of pure groundwater or pure glacier melt would serve as end members. However, for the purpose of this study, we focused on physicochemical signatures to distinguish between water that was probably of glacier origin, or on the other hand more resembling a groundwater signature. Hence, the choice was made to rely on the sites close to glaciers for the “glacier” end member and on lower altitude tributaries for the “groundwater” end member. The “glacier” end member was chosen based on geographical considerations as the average PC-1 score of the upmost sites 11 and 12. The “groundwater” end member was chosen as the average PC-1 score of tributaries 2, 4, and 7. This choice was based on the position of the tributaries in the space of principle components as well as on geographical considerations. The

fractions of glacier water and groundwater were then computed using the equations below:

$$f_{GM} = \frac{PC_{Sample} - PC_{GW}}{PC_{GM} - PC_{GW}} \quad (1)$$

$$f_{GW} = 1 - f_{GM} \quad (2)$$

where f_{GM} and f_{GW} are the estimated respective fractions of glacier meltwater (GM) and groundwater (GW), PC_{Sample} , PC_{GM} , PC_{GW} are the coordinates on the first principle component of respectively the sample in question, the glacier melt end member and the groundwater end member.

2.4.2 Analysis of nutrient concentrations

To assess the spatio-temporal control of the glaciers in the Valsorey catchment on stream nutrient concentrations, the measured values for phosphate (PO_4), ammonium (NH_4) and nitrate (NO_3) were plotted against the downstream distance from the snout of the Valsorey glacier separating the morning and afternoon samplings. A LOESS regression line was added to the plot for a better visual guidance. The differences between afternoon and morning values was also reported.

For a more compact comparison of the nutrient patterns and subsequent results, the catchment was divided in three zones based on noticeable differences in altitude and on landscape features. The highest zone (zone 3) encompassed the glaciers and the glacial floodplain, extending down to the canyon-like section. The second zone (zone 2) was marked by flatter terrain around the main stream which was joined by 5 tributaries. The limit of zone 2 was set by a steeper part further marking the transition to a zone of brush forest on the left bank of the main channel. From there on, Zone 1 extended down to the dam at the outlet of the catchment. Here the main stream was mostly flowing through extensive meadows. Using a two-way repeated measure analysis of variance (ANOVA), the morning to afternoon differences were assessed by zone. The statistical analysis was performed on log-transformed distributions in order to meet the assumption of normality. All

statistical tests were conducted using a significance level of 5 %. The software used was R version 4.0.4.

In a second step, the nutrient concentrations in the main channel were plotted against the fractions of glacier meltwater computed using the mixing model described in the previous subsection. To better assess the presence of a trend, a linear model was fitted and a correlation coefficient between the respective nutrient concentration and the percentage of glacier melt was computed. For these analyses, sites plotting out of the mixing space defined by the region of the first PCA axis lying between the defined end members were not considered.

2.4.3 Dissolved nitrogen stoichiometry: NH_4/NO_3

The influence of an increased glacier melt contribution to the streamflow in the main channel was expected to have an effect on the NH_4/NO_3 ratio in the main channel. Since the period of maximum glacier ablation coincides with a peak in dissolved NH_4 concentrations in (Tockner et al. 2002), we expected to see a higher NH_4/NO_3 ratio with increasing contribution of glacier melt to streamflow. To assess this, the mass concentrations of NH_4 and NO_3 first needed to be converted to molar concentrations in order for the N-fractions to be comparable. This was done by multiplying the mass concentrations by the respective molar weight of NH_4 (18 g/mol) and NO_3 (62 g/mol). Then, the resulting molar concentrations of NH_4 were divided by the NO_3 molar concentrations to obtain the NH_4/NO_3 ratio. Using the estimated fraction of glacier water as the x-axis, the ratios were plotted on a scatterplot and a linear regression was fitted. On the daily scale, the samples taken by the autosamplers were also analysed and the NH_4/NO_3 ratio was computed.

2.4.4 Export rates

To estimate nutrient export rates at the different sampling sites in the main channel, discharge measurements using salt releases were performed during both sampling campaigns in all tributaries as well as at 7 locations in the main channel (see figure in suppl. info). From

these locations, discharge at the sampling sites in the main channel was inferred by adding or subtracting the discharge from an inflowing tributary, according to hydrologic continuity at the confluence level. Potential infiltration or seepage of groundwater was therefore neglected. By multiplying the resulting discharge values with nutrient concentrations, nutrient mass fluxes (nutrient loads) were computed. These values were finally divided by the contributing subcatchment area at each sampling site to obtain nutrient export rates. Similarly to the analysis of nutrient concentrations, the export rates were plotted against the downstream location of the sampling sites in the main channel and differences between morning and afternoon were assessed. A two-way repeated measures ANOVA was applied to the log-transformed distributions of export rates to test for significant effects of either zone or sampling i.e. morning and afternoon differences.

2.4.5 Water and nutrient mass balance

On the scale of the entire catchment, the nutrient mass fluxes at the outlet of the catchment were compared with the fluxes of nutrients released by the different sources. For this purpose, the role of the three glaciers was considered separately while all non-glaciated tributaries were considered as one bulk source. First, the closure of the water balance was examined. The sum of the discharges from the sources was compared with the discharge at the catchment outlet. Then, a similar comparison was performed using the nutrient loads. This approach allowed for a rough scale analysis of the catchment’s role as a source or sink for the three analysed nutrients. For a better visual representation of the importance of the different sources, the nutrient loads were presented as proportions of the respective outlet nutrient fluxes.

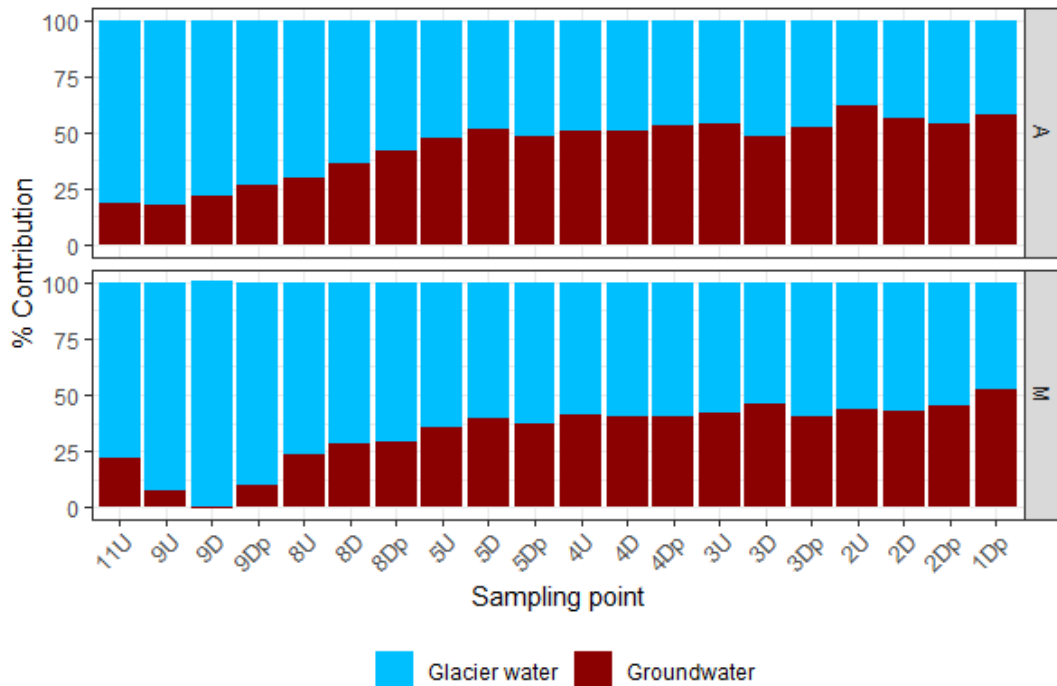


Figure 2: Contributions of glacier meltwater (light blue) and groundwater (dark red) to streamflow in the main channel as estimated by the two-end member mixing model. Top panel: A = Afternoon, bottom panel: M = Morning sampling. The sampling points are ordered according to their distance from the Valsorey glacier. Labelling follows the rule: site number followed by reach position (U = upstream of confluence, D = downstream of confluence, Dp = Downstream plus 50 m)

3 Results

3.1 Water source apportionment

In the plane of the two first PCA axes (cumulative explained variance of 65.5 %), the sampling points fell on a gradient along the first PC axis (explained variance: 48.9 %; Figure S2). High-altitude sites of the main channel closest to the glaciers yielded negative PC1 scores and tributaries encompassed the main channel sites on the positive PC1 side. While the clustering between main channel and tributary sites was dominant with the exception of tributary 7Te plotting in the cluster of main channel sites, the morning and afternoon samplings did plot close to each other for almost all sampling points. The first PCA axis (explained variance: 48.9 %) is dominated by the influence of the isotopic signal and by a

series of cations that exhibited strong correlation among themselves, namely calcium, sulphate, magnesium, and strontium. The second PCA axis (explained variance: 16.6 %) was mostly influenced by the sodium and chloride signal. Temperature, turbidity and potassium were less dominant on these axes (Table S1 for numerical data on measured streamwater physicochemical data).

The proportion of glacier water estimated by the end member mixing model ranged from almost 90 % in the upstream sites to 50 % in the lower altitude sites (Figure 2). While the proportion of groundwater increased significantly after the glacial floodplain, close to the downstream end of zone 1 (site 8), it only increased slightly in the lower zones to reach a plateau around 50 % contribution. The glacier water contribution was

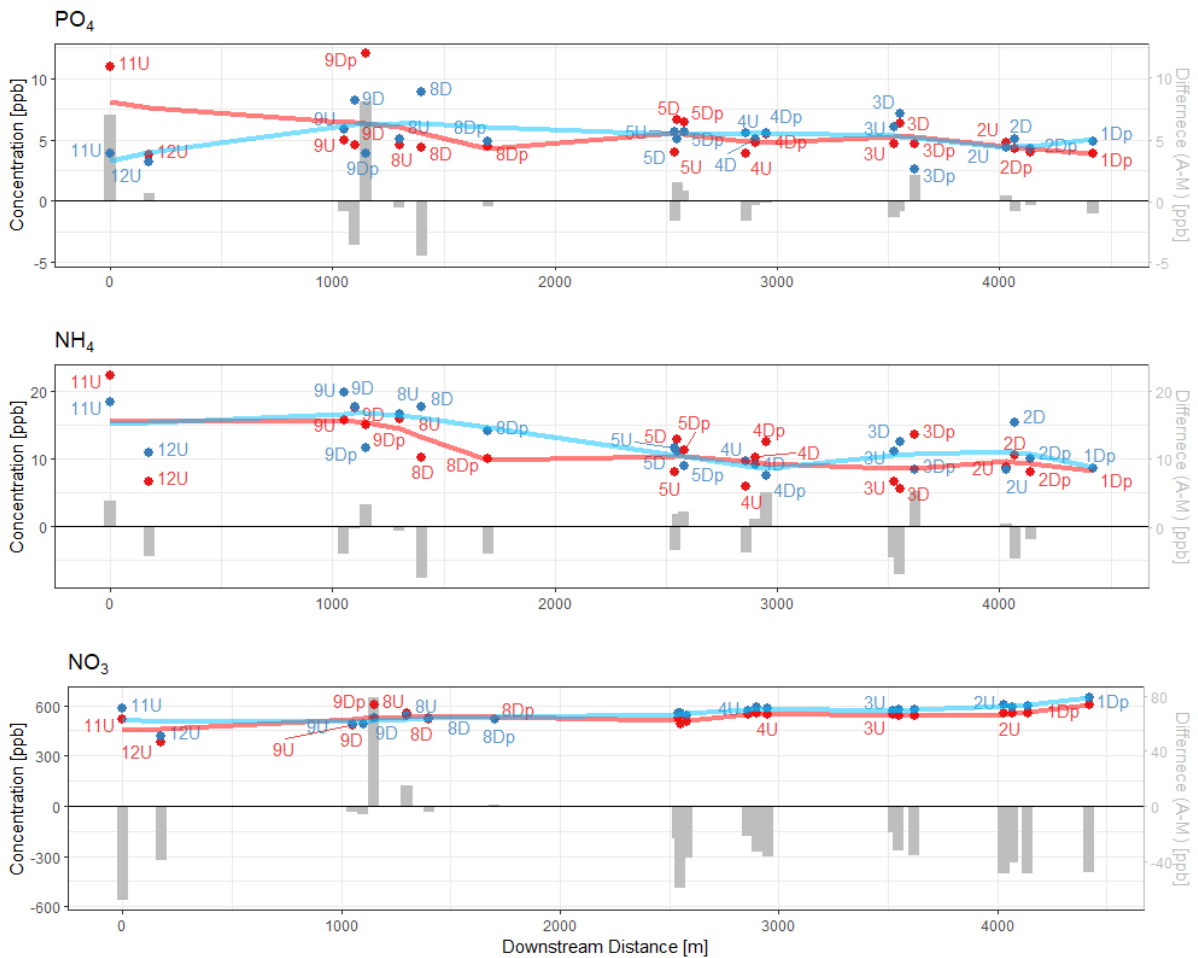


Figure 3: Measured nutrient concentrations at all main channel sites as a function of downstream distance from the Valsorey glacier snout (site 11). Lines show LOESS regression for morning (blue) and afternoon (red). Bars indicate afternoon – morning differences.

estimated slightly higher for the morning sampling compared to the afternoon sampling, although the differences between estimated morning and afternoon contributions remained small (mean of differences with respect to morning contributions of 16 %).

3.2 Dissolved nutrients concentration patterns

PO_4 and NH_4 exhibited a general decreasing longitudinal pattern while NO_x concentrations increased slightly with decreasing altitude (Figure 3). Overall, the nutrient concentrations did not vary substantially between afternoon and morning. At site 11U, the closest location to the Valsorey glacier snout, PO_4 showed a large daily variation, with the afternoon concentration being as high as twice the morning value (Figure 3). Nevertheless, this pattern was not exhibited by the sites close to the two other glaciers, although point 9Dp showed a large difference (the morning value was only 1/3 of the afternoon concentration), it was the only one at confluence 9 with this pattern. At 9D, located even closer to the confluence with the tributary flowing from the Tseudet glacier, the opposite difference was recorded. Similar observations could be made for NH_4 although differences in the upper zone were generally smaller than for PO_4 . While at site 11U, the afternoon value was slightly higher than the morning concentration (difference of 18 %), no such downstream pattern could be observed. The differences in NO_3 were small (< 10 %) throughout the catchment. In the lower reaches as well as in the most upstream ones, morning concentrations always plotted above afternoon values (usually a difference of approximately 7 %). The repeated measures ANOVA test found a significant effect from the zone for NH_4 and NO_3 , but no significant effect from the morning and afternoon samplings for all three nutrients.

PO_4 , NH_4 , and NO_3 concentrations showed varied responses with increasing glacier melt contribution to stream flow (Figure 4). Although some of the upstream sites (11U and 9Dp) exhibited considerably higher PO_4 compared to the bulk of the lower altitude sites, no general trend could be observed, and the correlation coefficient was weak $\rho = 0.34$; $p = 0.03$. On

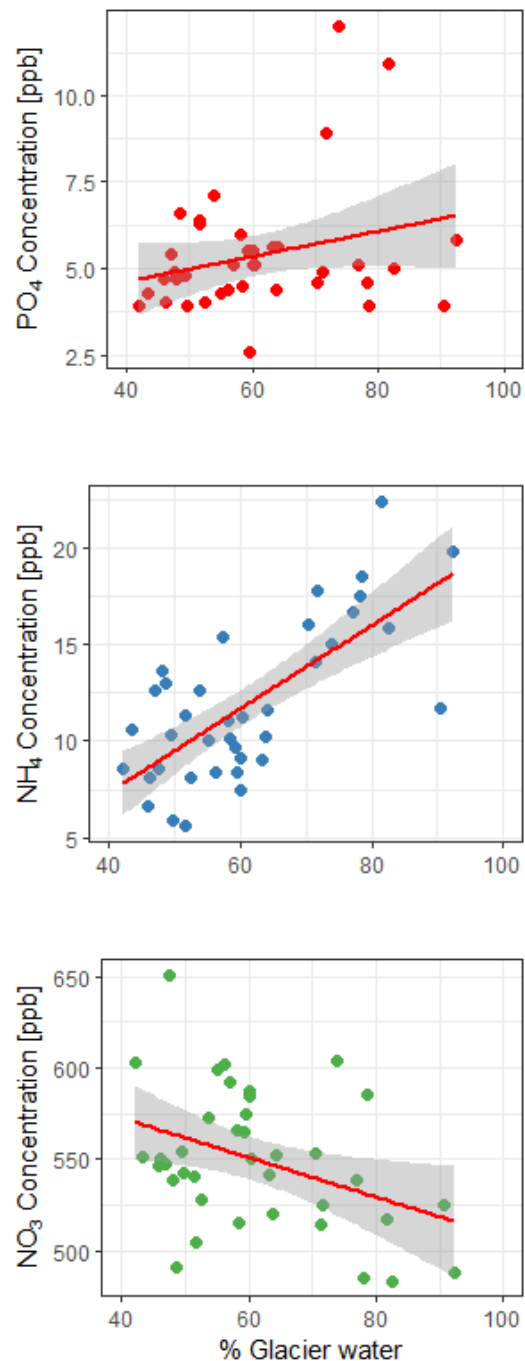


Figure 4: Nutrient concentrations as a function of glacier meltwater contribution to streamflow.

the other hand, the concentrations of NH_4 did show a relatively strong positive relationship with the percentage of glacier water and concentrations ranging between 5 and 23 ppb. Moreover, the linear model fitted to the data points was significant and the correlation coefficient was strong $\rho = 0.73$; $p = 1.1 \times 10^{-7}$. While measured NO_3 concentrations ranged between 450 and 650 ppb, an inverse relationship with the contribution of glacier

meltwater could be observed (Figure 4). Although the correlation coefficient was not strong $\rho = -0.43$; $p = 0.006$ a decreasing trend with increasing percentage of glacier melt emerged.

3.3 Dissolved nitrogen stoichiometry: NH_4/NO_3 patterns

As suggested by the behaviour of NH_4 and NO_3 , the NH_4/NO_3 ratio exhibited an increasing trend with growing contribution of glacier meltwater (Figure 5). The NH_4/NO_3 ratio increased from 0.04 to 0.15 as the fraction of glacier melt increased from 40 % to 92 %. The correlation coefficient of $\rho = 0.75$; $p = 2.6 \times 10^{-8}$ indicated a strong and significant link between these two variables. At the daily scale, the autosamplers revealed diel cycles in the NH_4/NO_3 ratio for the site closest to the Valsorey glacier (Figure S4). Here, the ratio increases from around 5-10 ppb during the morning hours to 15 ppb at 10 PM

and decreases again in the following hours. In the tributary 6T as well at the outlet of the catchment, no substantial cycle could be observed.

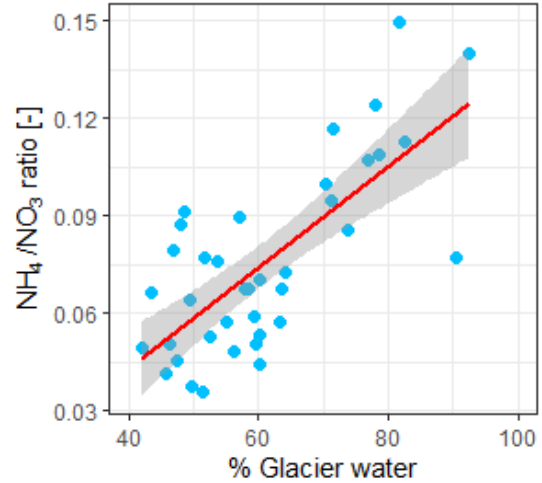


Figure 5: NH_4/NO_3 molar ratio as a function of glacier melt contribution to streamflow.

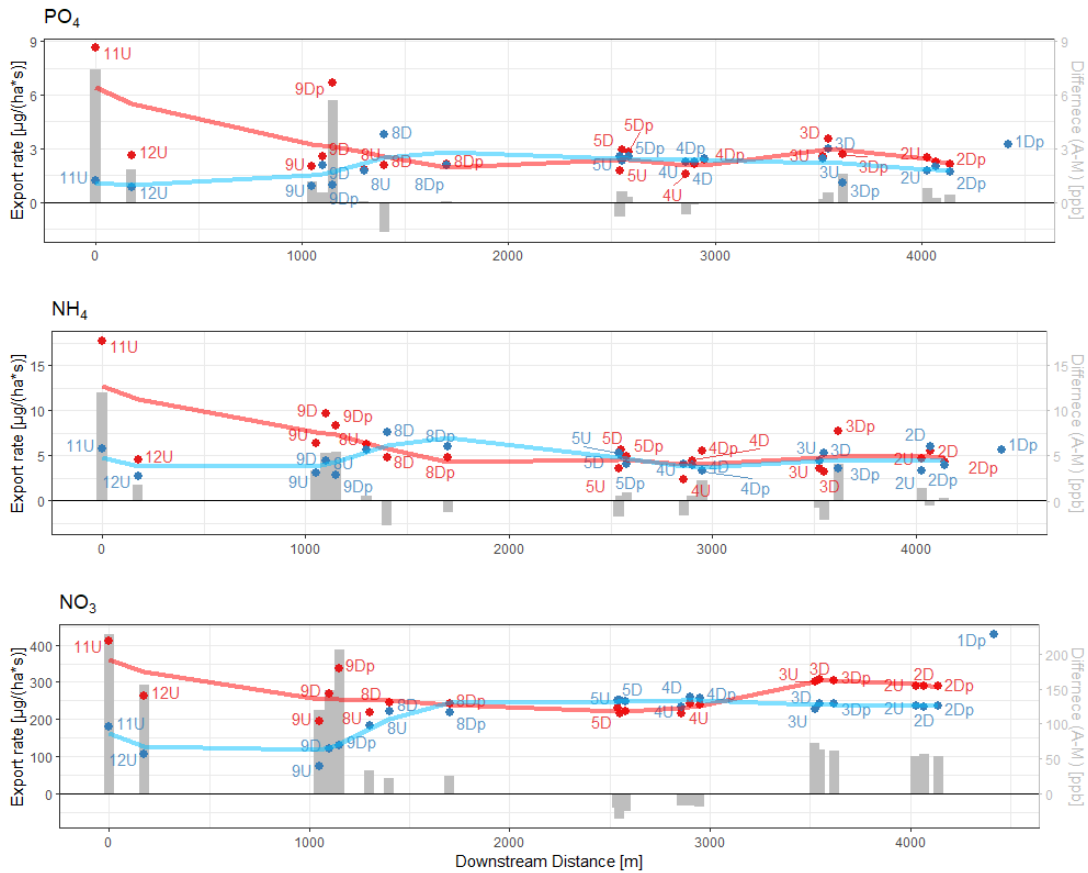


Figure 6: Export rates for each contributing subcatchment at all main channel sites as a function of downstream distance from the Valsorey glacier snout (site 11). Lines show LOESS regression for morning (blue) and afternoon (red). Bars indicate afternoon – morning differences.

3.4 Sub-catchment dissolved nutrients export

Afternoon and morning export rates for the different subcatchments generally showed a converging pattern as a function of downstream distance (Figure 6). While afternoon to morning differences were pronounced at the high-altitude sites close to the glaciers (up to 86 % at 11U for PO₄), these differences progressively faded. For all three nutrients, higher export rates close to the Valsorey glacier snout in the afternoon converged with morning rates around 1.5 km downstream distance. In the lower reaches, the afternoon to morning differences ranged around 15 % for PO₄ and around 20% for NO₃ with afternoon values consistently plotting above morning rates. NH₄ export rates did not show a consistent pattern in the lower reaches and the magnitude of differences was also variable with local differences around 20 % to 50 %. The two-way repeated measures ANOVA indicated a significant sampling effect for PO₄ and NO₃. Additionally, the test yielded a significant combined effect of sampling and

zone for PO₄ and NO₃. For NH₄, no significant effect was found.

3.5 Catchment scale mass balance

The water balance between the water sources to the Torrent du Valsorey and the outlet of the catchment was not entirely closed. In the afternoon a difference of 253 litres and in the morning 287 litres was measured at the outlet of the catchment compared to the sum of the measured source discharges (Table 1). Nevertheless, a proportion of 80 % in the afternoon and 70 % in the morning of the outlet discharge was measured at the inflows into the main channel. The most important sources of water to the main channel in terms of discharge were the tributaries considered as a bulk source, followed by the Valsorey glacier, the Tseudet and the Sonadon glacier. However, the sum of glacier discharges in the afternoon exceeded the discharge from the sum of tributaries. Regarding the nutrient loads, the

Location		Sampling	Discharge [m ³ /s]	PO ₄ load [mg/s]	NH ₄ load [mg/s]	NO ₃ load [mg/s]
Glacier-fed sources	Glacier du Valsorey (Site 11)	A	283	3.1	6.3	146.0
		M	110	0.4	2.0	64.6
	Glacier du Sonadon (Site 12)	A	167	0.6	1.1	63.2
		M	62	0.2	0.7	25.8
	Glacier du Tseudet (Site 9)	A	170	1.1	1.8	111.6
		M	106	0.3	1.4	71.9
Sum of glacier-fed sources		A	620	4.8	9.3	320.8
		M	277	0.9	4.1	162
All other tributaries		A	401	2.2	4.2	229.2
		M	391	2.2	3.9	223.2
Outlet		A	1274	5.1	10.3	701.3
		M	956	4.1	9.6	572.8

Table 1: Nutrient loads for the different water sources to the main stream. Glacier-fed streams are considered separately. Sampling indicates afternoon (A) or morning (M) campaign.

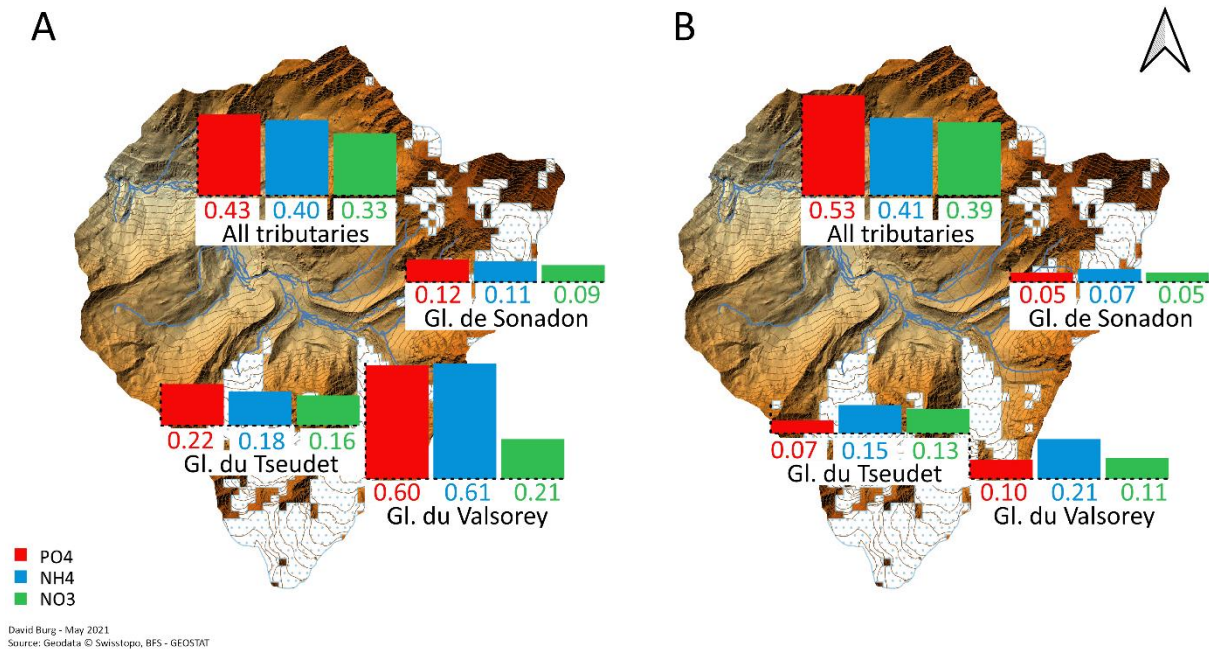


Figure 7: Fraction of nutrient mass fluxes (loads) with respect to nutrient fluxes at the outlet for afternoon (panel A) and morning (panel B).

bulk tributaries exhibited a rather constant and important source of nutrients to the main stream while the morning to afternoon variation for the glaciers was large (Figure 7). The largest differences were exhibited by the Valsorey glacier (up to 50 % difference for PO₄, Figure 7) but the Tseudet and the Sonadon glacier also showed such differences although they were smaller in magnitude (up to 15 % difference for PO₄ for the Tseudet glacier). In the afternoon, the highest loads of PO₄ and NH₄ to the main channel originated at the Valsorey glacier but the highest load of NO₃ came from the tributaries. In the morning, the nutrient flux released by each of the glaciers was minor compared to the flux coming from the tributaries. Considered together, the glacier-fed sources released a much higher flux of PO₄ (+118 %), NH₄ (+121 %), and NO₃ (+40 %) in the afternoon compared to the bulk tributaries. In the morning however, this difference faded or was inverted: PO₄ (-60 %), NH₄ (+5 %) and NO₃ (-27 %). From a perspective of mass balance, the sources released 37 % more PO₄, and 30 % more NH₄ than the measured respective loads at the outlet. However, 20 % of the NO₃ flux at the outlet could not be explained by the sum of source fluxes.

4 Discussion

4.1 Glacier control on stream nutrient dynamics

The synoptic sampling carried out in this study demonstrates that glaciers within the Valsorey catchment represent point-sources of inorganic nitrogen to downstream fluvial ecosystems. Consistent with previous studies highlighting this role, the ranges of measured stream NH₄-N and NO₃-N concentrations in the studied catchment are comparable to values reported from other glaciated mountain catchments. NH₄-N concentrations in the main channel are close to values measured in the Val Roseg for glacial meltwater (Tockner et al. 2002) and NO₃-N values are slightly lower than those reported in Val Roseg but close to those measured downstream of the Indren glacier in the Valle d'Aosta region of the Italian alps (Colombo et al. 2019), just about 50 km from Valsorey. Further away, NH₄-N concentrations from Valsorey are also close to concentrations measured at the Leverett glacier in Greenland during the 2012 melting season (Wadham et al. 2016). Moreover, in terms of nutrient loads, our results highlight the importance of glacier-fed streams as nutrient sources compared to other

mostly groundwater-fed tributaries. The substantially higher nutrient loads in glacier-fed streams in the afternoon thus contribute to the heterogeneity of high-mountain ecosystems.

Further, our results indicate that melting glaciers not only influence the abundance of individual nutrient forms but exert a control on their relative proportions leading to a higher NH_4/NO_3 ratio in the stream reaches that are most influenced by glacial meltwater (Figure 5). In the seasonal patterns found by (Tockner et al. 2002), peak NO_3 concentrations during late spring are followed by high NH_4 concentrations during summer. Such observations coincide with observations from the long-term Metalp monitoring program in Valsorey ('METALP DATA PORTAL' 2020). Our results thus consolidate the concept that glaciers, besides acting as sources of high amounts of NO_3 , also act as sources of reduced N- NH_4 to downstream ecosystems. This shift in the stoichiometry of N species throughout the melting season may influence microbial communities of glacier-fed streams as NH_4 is an energetically cheaper source of N compared to NO_3 (Naldi and Wheeler 1999). Differences in NH_4/NO_3 ratio also may reflect possible changes in redox conditions that subsequently impact the cycling of nitrogen within the stream. Under reducing conditions that may be present in the streambed sediments, the demand for NO_3 is very high as it is the energetically most suitable electron acceptor under anoxic conditions. Although the implications of changing NH_4/NO_3 ratios in high-mountain streams are understudied, NH_4 may lead to higher nitrification by stream biota but the NH_4 uptake by stream communities is linked to complex site-specific interactions making general predictions difficult (Day and Hall 2017).

The synoptic sampling carried out in Valsorey not only lead to a general characterization of glacier influence on stream nutrient dynamics but further allowed for a differentiated comparison of the impact exerted by the three glaciers in the catchment. Our results highlight that glaciers can vary considerably in their contribution to stream nutrient dynamics. Indeed, the stream coming from the snout of the Valsorey glacier (site 11) contains higher PO_4

and NH_4 concentrations compared to the ones flowing from the Sonadon and Tseudet glaciers (Figure 7). However, this finding might be distorted by the distances between the sampling positions and the glaciers which were longer for the Sonadon (site 12) and Tseudet (site 9) glaciers. Still, the variation between sites 11 and 12 regarding PO_4 and NH_4 is large considering the values from other sites within the catchment, thus stressing that not only glaciated environments but glaciers per se are heterogeneous environments. Since atmospheric N-deposition rates can probably be considered constant over the catchment area according to modelled deposition data (Rihm and Künzle 2019), considering local influences such as the underlying geology, variations in meltwater pathways across the englacial environment, or the differentiated influence exerted by microbial processes is possibly of major importance.

In the context of retreating glaciers, assessing the longitudinal extent of glacier influence in the stream nutrient patterns is important in order to predict upcoming changes for the ecosystems of glacier-fed streams. Stream biota that has adapted to diel cycles related to glacier dynamics will be subject to a decreasing magnitude of daily variations as the glaciers progressively vanish. From our results, we are able to observe the downstream distance at which patterns from morning and afternoon samplings converge, which results in two possibilities. While the nutrient concentrations (Figure 3) suggest that in the afternoon, the melting Valsorey glacier lead to higher NH_4 values only very close to its snout, the export rates (Figure 6) point at a longer distance of about 1.5 km downstream. Regarding NO_3 , concentrations suggest slightly less nitrate with increasing proximity to the glacier snout, but export rates indicate a similar distance as for NH_4 . Concentrations have the inconvenience of potentially being affected by a dilution effect with increasing discharge but considering export rates adds the uncertainties associated with the discharge measurements. Thus, these considerations do not allow for an unambiguous evaluation of the longitudinal extent of glacier influence on stream nutrient concentrations. A

finer resolution in the sampling at short distances from the glaciers is needed to elucidate this question.

At catchment scale, the general nutrient mass balance with respect to the main stream reveals that the main stream acts as a sink for PO_4 and NH_4 . As the mass balance for NO_3 could not be closed there must be other sources contributing to the NO_3 load at the catchment outlet. Since subsurface groundwater inflows (e.g., aquifer water) are neglected by the chosen mass balance approach and since the water balance is not closed either, groundwater inflows to the main channel are likely to contribute to the NO_3 load. NO_3 concentrations in lower-altitude tributaries in Valsorey as well as NO_3 concentrations from hillslope groundwater in the Val Roseg (Tockner et al. 2002) consolidate this idea.

4.2 Possible origin and fate of stream nutrients

NO_3 probably finds its way onto the glacier surfaces via atmospheric deposition, a process that is potentially important in this region of the European Alps as many industrial and agricultural activities are taking place in nearby regions (Brighenti et al. 2019; Ren et al. 2019). The weathering action of the glaciers on the underlying rocks could imply another source of nitrogen to the subglacial environment (Houlton, Morford, and Dahlgren 2018). However, other phenomena such as reduced contact with soils, permafrost thaw or microbial production are probably also contributing to the high NO_3 concentrations commonly observed in high-mountain environments (Brighenti et al. 2019; Colombo et al. 2019; Ren et al. 2019). Indeed, nitrogen from rock weathering in the form of NH_4 attached to sediments could then serve as substrate for nitrifying bacteria thus enriching glacial melt in NO_3 (Hodson et al. 2008). However, nitrate-reducing bacteria that have been found in sediments beneath glaciers of the northern and southern hemisphere could catalyse the transformation of the weathered N to NH_4 that could then be flushed to the glacier-fed stream (Foght et al. 2004). These different hypotheses indicate that Although the precise

pathways by which microorganisms act on the complex biogeochemistry of nitrogen in glacier melt are not well understood, a microbial implication in some of the reactions is most probable (Hodson et al. 2008). The source of phosphate to glacier-fed streams is likely to be associated with the erosion of subglacial rocks although the contribution of glacial environments to stream PO_4 remains understudied (Brighenti et al. 2019; Hodson 2006).

After their release from the cryospheric reservoirs, streamwater nutrients may be taken up by stream biofilms, algae, and plants. As these communities are usually nutrient-limited, nutrients of glacier origin sustain primary production and microbial diversity in the glacier-fed stream (Kohler et al. 2016). However, other characteristics of glacier-fed streams such as high turbidity may diminish the uptake capacity of these communities (Ren et al. 2019). Our results suggest a rapid uptake or transformation of NH_4 and PO_4 as their concentrations are rapidly decreasing in the afternoon but the high and longitudinally increasing NO_3 concentrations may indicate nitrification and an overabundance in NO_3 in the main stream.

5 Conclusion

Owing to climate change, mountain glaciers are rapidly retreating worldwide but their role in high-altitude environments as well as their control on downstream ecosystems remain understudied (Milner et al. 2017). Here, we investigated the spatio-temporal control that glaciers exert on stream nutrients in a partially glaciated mountain catchment. By correlating glacier melt contributions to streamwater with observed nutrient concentrations, we highlight the importance of glaciers as sources of nutrients to glacier-fed streams in environments that are often nutrient limited (Robinson and Gessner 2000). Moreover, a mass balance approach suggests that glaciers do not uniformly release nutrients, even at catchment scale thus stressing the importance to further investigate the processes in the glacier ecosystem leading to nutrient release. Such

processes are likely to involve microorganisms but may also be due to the physicochemical weathering forces of glaciers. Finally, results from this study also suggest that further research is needed to understand how and when nutrients supplied by glaciers are utilized and transformed within high-mountain landscapes.

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References

- Bodenbedeckung*. 2019. 11087256. Neuchâtel: BFS.
<https://www.bfs.admin.ch/hub/api/dam/assets/11087256/master>.
- Brighenti, Stefano, Monica Tolotti, Maria Cristina Bruno, Geraldene Wharton, Martin T. Pusch, and Walter Bertoldi. 2019. 'Ecosystem Shifts in Alpine Streams under Glacier Retreat and Rock Glacier Thaw: A Review'. *Science of The Total Environment* 675 (July): 542–59.
<https://doi.org/10.1016/j.scitotenv.2019.04.221>.
- Canadell, Marta Boix, Nicolas Escoffier, Amber J. Ulseth, Stuart N. Lane, and Tom J. Battin. 2019. 'Alpine Glacier Shrinkage Drives Shift in Dissolved Organic Carbon Export From Quasi-Chemostasis to Transport Limitation'. *Geophysical Research Letters* 46 (15): 8872–81.
<https://doi.org/10.1029/2019GL083424>.
- Christophersen, Nils, and Richard P. Hooper. 1992. 'Multivariate Analysis of Stream Water Chemical Data: The Use of Principal Components Analysis for the End-Member Mixing Problem'. *Water Resources Research* 28 (1): 99–107.
<https://doi.org/10.1029/91WR02518>.
- Colombo, Nicola, Daniele Bocchiola, Maria Martin, Gabriele Confortola, Franco Salerno, Danilo Godone, Michele Eugenio D'Amico, and Michele Freppaz. 2019. 'High Export of Nitrogen and Dissolved Organic Carbon from an Alpine Glacier (Indren Glacier, NW Italian Alps)'. *Aquatic Sciences* 81 (4): 74.
<https://doi.org/10.1007/s00027-019-0670-z>.
- Conley, D. J., H. W. Paerl, R. W. Howarth, D. F. Boesch, S. P. Seitzinger, K. E. Havens, C. Lancelot, and G. E. Likens. 2009. 'ECOLOGY: Controlling Eutrophication: Nitrogen and Phosphorus'. *Science* 323 (5917): 1014–15.
<https://doi.org/10.1126/science.1167755>.
- Day, Natalie K., and Robert O. Hall. 2017. 'Ammonium Uptake Kinetics and Nitrification in Mountain Streams'. *Freshwater Science* 36 (1): 41–54.
<https://doi.org/10.1086/690600>.
- Foght, J., J. Aislabie, S. Turner, C. E. Brown, J. Ryburn, D. J. Saul, and W. Lawson. 2004. 'Culturable Bacteria in Subglacial Sediments and Ice from Two Southern Hemisphere Glaciers'. *Microbial Ecology* 47 (4): 1036–5.
<https://doi.org/10.1007/s00248-003-1036-5>.
- Gardner, Alex S., Geir Moholdt, J. Graham Cogley, Bert Wouters, Anthony A. Arendt, John Wahr, Etienne Berthier, et al. 2013. 'A Reconciled Estimate of Glacier Contributions to Sea Level Rise: 2003 to 2009'. *Science* 340 (6134): 852–57.
<https://doi.org/10.1126/science.1234532>.
- Gordon, Nancy, Thomas McMahon, Brian Finlayson, Christopher Gippel, and Nathan Rory. 2004. *Stream Hydrology: An Introduction for Ecologists*. Chichester: John Wiley & Sons, Ltd.
<https://www.wiley.com/en-us/Stream+Hydrology%3A+An+Intro>

- ction+for+Ecologists%2C+2nd+Edition-
p-9780470843581.
- Hallet, B., Lewis Hunter, and Jim Bogen. 1996. 'Rates of Erosion and Sediment Evacuation by Glaciers: A Review of Field Data and Their Implications'. *Global and Planetary Change* 12 (March): 213–35. [https://doi.org/10.1016/0921-8181\(95\)00021-6](https://doi.org/10.1016/0921-8181(95)00021-6).
- Hodson, Andy. 2006. 'Phosphorus in Glacial Meltwaters'. In *Glacier Science and Environmental Change*, 81–82. John Wiley & Sons, Ltd. <https://doi.org/10.1002/9780470750636.ch17>.
- Hodson, Andy, Alexandre M. Anesio, Martyn Tranter, Andrew Fountain, Mark Osborn, John Priscu, Johanna Laybourn-Parry, and Birgit Sattler. 2008. 'GLACIAL ECOSYSTEMS'. *Ecological Monographs* 78 (1): 41–67. <https://doi.org/10.1890/07-0187.1>.
- Hood, Eran, Tom J. Battin, Jason Fellman, Shad O'Neel, and Robert G. M. Spencer. 2015. 'Storage and Release of Organic Carbon from Glaciers and Ice Sheets'. *Nature Geoscience* 8 (2): 91–96. <https://doi.org/10.1038/ngeo2331>.
- Hooper, Richard P. 2003. 'Diagnostic Tools for Mixing Models of Stream Water Chemistry'. *Water Resources Research* 39 (3). <https://doi.org/10.1029/2002WR001528>.
- Hooper, Richard P., Nils Christophersen, and Norman E. Peters. 1990. 'Modelling Streamwater Chemistry as a Mixture of Soilwater End-Members — An Application to the Panola Mountain Catchment, Georgia, U.S.A.'. *Journal of Hydrology, Transfer of Elements Through the Hydrological Cycle*, 116 (1): 321–43. [https://doi.org/10.1016/0022-1694\(90\)90131-G](https://doi.org/10.1016/0022-1694(90)90131-G).
- Houlton, B. Z., S. L. Morford, and R. A. Dahlgren. 2018. 'Convergent Evidence for Widespread Rock Nitrogen Sources in Earth's Surface Environment'. *Science* 360 (6384): 58–62. <https://doi.org/10.1126/science.aan4399>.
- Hungate, Bruce A., Jeffrey S. Dukes, M. Rebecca Shaw, Yiqi Luo, and Christopher B. Field. 2003. 'Nitrogen and Climate Change'. *Science* 302 (5650): 1512–13. <https://doi.org/10.1126/science.1091390>.
- Kohler, Tyler J., David J. Van Horn, Joshua P. Darling, Cristina D. Takacs-Vesbach, and Diane M. McKnight. 2016. 'Nutrient Treatments Alter Microbial Mat Colonization in Two Glacial Meltwater Streams from the McMurdo Dry Valleys, Antarctica'. *FEMS Microbiology Ecology* 92 (4). <https://doi.org/10.1093/femsec/fiw049>.
- Koppes, Michèle N. 2020. 'Rates and Processes of Glacial Erosion'. In *Reference Module in Earth Systems and Environmental Sciences*. Elsevier. <https://doi.org/10.1016/B978-0-12-818234-5.00032-8>.
- 'METALP DATA PORTAL'. 2020. <https://metalp-data.epfl.ch/>.
- Milner, Alexander M., Kieran Khamis, Tom J. Battin, John E. Brittain, Nicholas E. Barrand, Leopold Fuehrer, Sophie Cauvy-Fraunie, et al. 2017. 'Glacier Shrinkage Driving Global Changes in Downstream Systems'. *Proceedings of the National Academy of Sciences of the United States of America* 114 (37): 9770–78. <https://doi.org/10.1073/pnas.1619807114>.
- Naldi, Mariachiara, and Patricia A. Wheeler. 1999. 'Changes in Nitrogen Pools in *Ulva Fenestrata* (Chlorophyta) and *Gracilaria Pacifica* (Rhodophyta) Under Nitrate and Ammonium Enrichment'. *Journal of Phycology* 35 (1): 70–77. <https://doi.org/10.1046/j.1529-8817.1999.3510070.x>.
- Peterson, Bruce J., Wilfred M. Wollheim, Patrick J. Mulholland, Jackson R. Webster, Judy L. Meyer, Jennifer L. Tank, Eugènia Martí, et al. 2001. 'Control of Nitrogen Export from Watersheds by Headwater Streams'. *Science* 292 (5514): 86–90.

- <https://doi.org/10.1126/science.1056874>.
- Ren, Ze, Nicolas Martyniuk, Isabella A. Oleksy, Anshuman Swain, and Scott Hotaling. 2019. 'Ecological Stoichiometry of the Mountain Cryosphere'. *Frontiers in Ecology and Evolution* 7. <https://doi.org/10.3389/fevo.2019.00360>.
- Rihm, Beat, and Thomas Künzle. 2019. 'Mapping Nitrogen Deposition 2015 for Switzerland'. Meteotest AG, commissioned by Federal Office for the Environment (FOEN). <https://www.bafu.admin.ch/dam/bafu/en/dokumente/luft/externe-studien-berichte/mapping-nitrogen-deposition-2015-for-switzerland.pdf.download.pdf/Mapping%20Nitrogen%20Deposition%202015%20for%20Switzerland.pdf>.
- Robinson, C. T., and M. O. Gessner. 2000. 'Nutrient Addition Accelerates Leaf Breakdown in an Alpine Springbrook'. *Oecologia* 122 (2): 258–63. <https://doi.org/10.1007/PL00008854>.
- Singer, Gabriel A., Christina Fasching, Linda Wilhelm, Jutta Niggemann, Peter Steier, Thorsten Dittmar, and Tom J. Battin. 2012. 'Biogeochemically Diverse Organic Matter in Alpine Glaciers and Its Downstream Fate'. *Nature Geoscience* 5 (10): 710–14. <https://doi.org/10.1038/ngeo1581>.
- Tockner, Klement, Florian Malard, Urs Uehlinger, and J. V. Ward. 2002. 'Nutrients and Organic Matter in a Glacial River—Floodplain System (Val Roseg, Switzerland)'. *Limnology and Oceanography* 47 (1): 266–77. <https://doi.org/10.4319/lo.2002.47.1.0266>.
- Tranter, M., M. J. Sharp, H. R. Lamb, G. H. Brown, B. P. Hubbard, and I. C. Willis. 2002. 'Geochemical Weathering at the Bed of Haut Glacier d'Arolla, Switzerland—a New Model'. *Hydrological Processes* 16 (5): 959–93. <https://doi.org/10.1002/hyp.309>.
- Wadham, Jemma Louise, Jonathan Hawkings, Jon Telling, Dave Chandler, Jon Alcock, Emily O'Donnell, Preeti Kaur, et al. 2016. 'Sources, Cycling and Export of Nitrogen on the Greenland Ice Sheet'. *Biogeosciences* 13 (22): 6339–52. <https://doi.org/10.5194/bg-13-6339-2016>.
- Ward, J. V. 1989. 'The Four-Dimensional Nature of Lotic Ecosystems'. *Journal of the North American Benthological Society* 8 (1): 2–8. <https://doi.org/10.2307/1467397>.

Supplementary information to:

The role of glaciers as sources of stream
nutrients in a high mountain catchment

Supplementary Tables

Sampling point ID	Sampling	Zone	DO %	Streamwater temperature [°C]	pH	Electrical conductivity [uS/cm]	Turbidity [NTU]	DOC [ppb]	$\delta^{18}\text{O}$ VSMOW	δD VSMOW	Cl [ppm]	SO4 [ppm]	Na [ppm]	Mg [ppm]	K [ppm]	Ca [ppm]	Sr [ppm]	PO4 [ppb]	NH4 [ppb]	Nox [ppb]
11U	A	3	100.5	0.2	7.17	231	213.5	86.7	-14.227	-101.181	0.104	66.938	1.251	5.301	1.853	35.998	0.226	10.9	22.4	516.8
11U	M	3	99.8	0.2	7.92	264	98.0	102.0	-14.115	-100.615	0.100	79.339	1.393	6.341	2.012	40.900	0.252	3.9	18.5	585.0
12U	A	3	100.0	6.1	7.31	424	63.4	51.7	-14.157	-102.428	0.163	155.037	0.865	14.796	0.647	65.396	0.471	3.8	6.6	378.6
12U	M	3	99.6	3.5	8.00	364	20.8	56.3	-14.102	-102.070	0.204	188.703	0.919	17.378	0.591	74.964	0.529	3.2	10.9	418.3
9U	A	3	100.2	8.5	8.18	316	142.1	68.3	-14.004	-100.556	0.138	56.292	1.271	7.444	0.990	32.732	0.187	5.0	15.8	483.6
9U	M	3	98.5	1.8	7.81	360	98.5	72.3	-14.095	-101.132	0.228	66.470	1.385	8.604	0.995	36.317	0.209	5.8	19.8	487.9
9D	A	3	99.8	8.5	8.13	310	665.7	111.0	-14.047	-100.340	0.265	61.679	1.482	8.368	1.031	34.502	0.205	4.6	17.5	485.5
9D	M	3	99.7	1.8	7.79	356	92.6	69.7	-14.071	-100.723	0.162	75.745	1.264	9.071	0.998	38.639	0.228	8.2	17.8	492.1
9T	A	3	100.4	6.0	7.74	184	55.4	123.0	-13.880	-98.654	0.138	56.856	1.273	7.429	0.986	32.510	0.197	6.6	10.9	654.6
9T	M	3	99.5	1.6	7.47	210	21.1	95.7	-13.807	-98.133	0.099	71.505	1.255	8.873	0.981	37.935	0.224	2.7	13.3	679.9
9Dp	A	3	99.9	8.3	8.17	295	123.0	76.3	-14.012	-100.088	0.127	6.815	1.292	3.410	0.548	21.113	0.080	12.0	15.0	604.1
9Dp	M	3	99.9	1.8	7.90	331	103.4	77.3	-14.038	-100.438	0.113	6.456	1.283	3.363	0.526	20.420	0.080	3.9	11.7	524.9
8U	A	3	100.2	8.1	8.10	300	62.4	91.0	-14.014	-100.299	0.141	58.829	1.317	8.019	1.009	32.841	0.192	4.6	16.0	553.2
8U	M	3	100.0	7.2	8.01	312	62.2	120.0	-14.023	-100.324	0.557	69.198	1.619	8.617	0.938	36.824	0.219	5.1	16.7	538.5
8T2	A	3	99.4	10.4	8.31	241	1.6	256.0	-14.021	-101.363	0.265	58.137	1.499	7.716	1.273	33.118	0.214	5.7	10.5	394.6
8T2	M	3	100.7	11.2	7.81	253	4.2	243.0	-13.987	-101.078	0.120	71.346	1.299	8.821	0.958	36.883	0.221	5.5	8.7	397.7
8D	A	3	100.7	7.9	8.13	277	42.8	107.0	-14.036	-100.293	0.216	57.815	1.336	7.510	1.007	32.604	0.218	4.4	10.2	520.1
8D	M	3	100.5	7.7	7.92	293	89.4	96.7	-13.957	-99.944	0.111	72.671	1.276	9.031	0.990	37.999	0.278	8.9	17.8	524.7
8T1	A	3	99.4	10.4	8.31	241	NA	141.0	-14.016	-101.127	0.085	12.939	1.222	4.251	0.458	16.841	0.066	6.1	12.8	500.1
8T1	M	3	98.1	10.1	7.74	210	1.8	133.0	-13.951	-100.679	0.085	12.838	1.223	4.322	0.455	16.931	0.058	4.7	14.0	512.8
8Dp	A	2	95.0	9.0	8.27	270	33.7	101.0	-13.945	-99.926	0.133	59.647	1.287	7.705	1.026	32.796	0.213	4.5	10.1	515.3
8Dp	M	2	98.5	3.8	7.02	303	19.2	85.3	-14.005	-100.245	0.740	71.420	1.776	8.887	1.016	37.072	0.226	4.9	14.1	514.2
7T	A	2	96.1	7.1	7.86	87.8	2.8	181.0	-13.641	-98.168	0.102	64.953	1.296	8.689	1.061	35.021	0.231	5.3	9.4	515.1
7T	M	2	99.3	6.2	7.21	86.6	0.7	53.7	-13.687	-98.138	0.113	82.127	1.275	9.512	1.047	40.261	0.249	7.4	8.8	502.9
7Te	A	2	95.8	3.2	8.34	266	2.3	85.3	-14.203	-102.468	0.099	62.914	1.292	8.606	1.063	34.753	0.224	6.5	15.4	580.0
7Te	M	2	98.8	3.0	7.01	266	0.9	184.0	-14.165	-101.867	0.109	78.441	1.271	9.435	1.038	39.968	0.237	6.6	7.7	585.6
6T	A	2	93.5	6.7	8.14	184.9	2.1	199.0	-13.835	-99.754	0.119	23.384	1.536	5.883	0.647	18.464	0.060	5.9	10.3	448.5
6T	M	2	95.0	8.0	NA	184	0.8	221.0	-13.876	-99.706	0.111	26.557	1.547	6.115	0.653	19.902	0.090	5.6	11.9	435.3
5U	A	2	97.9	9.5	8.20	257	14.2	109.0	-13.965	-100.283	0.100	63.912	1.258	8.526	1.071	34.820	0.220	4.0	8.1	527.8
5U	M	2	94.8	3.2	8.19	285	16.7	100.0	-13.950	-100.347	0.098	78.379	1.226	9.386	1.031	39.995	0.246	5.6	11.6	551.9
5D	A	2	98.0	9.2	8.23	257	13.8	127.0	-13.915	-99.726	0.161	67.807	1.327	8.669	1.080	35.936	0.235	6.6	13.0	490.5
5D	M	2	94.6	3.2	8.22	285	14.0	92.3	-13.880	-99.745	0.593	81.862	1.584	9.268	1.064	38.300	0.254	5.1	11.2	550.1
5T	A	2	97.9	11.3	7.56	359	NA	558.0	-13.233	-96.662	0.109	67.930	1.281	8.967	1.139	36.837	0.243	5.2	7.1	84.8
5T	M	2	94.1	7.0	7.63	368	0.8	554.0	-13.257	-96.833	0.112	84.221	1.263	9.820	1.100	41.882	0.246	3.1	13.5	133.3

Sampling point ID	Sampling	Zone	DO %	Streamwater temperature [°C]	pH	Electrical conductivity [uS/cm]	Turbidity [NTU]	DOC [ppb]	$\delta^{18}\text{O}$ VSMOW	δD VSMOW	Cl [ppm]	SO ₄ [ppm]	Na [ppm]	Mg [ppm]	K [ppm]	Ca [ppm]	Sr [ppm]	PO ₄ [ppb]	NH ₄ [ppb]	Nox [ppb]
5Dp	A	2	97.3	8.7	8.24	253	11.4	125.0	NA	NA	0.093	0.467	0.980	0.987	0.182	6.552	NA	6.4	11.3	504.4
5Dp	M	2	93.4	3.4	8.19	285	13.5	86.0	-13.959	-100.134	0.105	0.507	1.000	1.017	0.279	6.726	0.027	5.6	9.0	542.0
4U	A	2	102.7	8.0	8.23	246	12.1	116.0	-13.969	-100.222	0.100	69.288	1.252	8.861	1.113	36.553	0.242	3.9	5.9	542.9
4U	M	2	103.6	3.4	8.23	278	11.7	110.0	-13.926	-100.153	0.102	82.754	1.237	9.700	1.055	41.358	0.271	5.5	9.7	564.9
4D	A	2	98.1	7.3	8.14	240	9.5	143.0	-13.939	-99.917	0.597	34.563	1.804	7.860	0.770	24.734	0.149	4.8	10.3	554.6
4D	M	2	98.5	3.6	8.21	270	12.3	105.0	-13.938	-99.972	0.394	35.041	1.699	7.887	0.768	25.282	0.176	5.1	9.1	587.8
4T	A	2	96.7	5.9	8.01	137.8	NA	144.0	-13.638	-97.700	0.084	16.641	1.252	3.185	0.602	12.644	0.054	4.1	5.5	843.9
4T	M	2	95.8	9.1	NA	147.1	3.8	109.0	-13.571	-97.639	0.082	16.982	1.232	3.071	0.574	12.237	0.062	3.6	6.5	877.0
4Dp	A	2	97.4	7.5	8.12	241	10.4	104.0	-13.883	-99.862	0.084	55.103	1.566	12.981	0.924	35.043	0.276	5.4	12.6	547.3
4Dp	M	2	98.5	3.6	8.21	271	10.2	114.0	-13.989	-100.135	0.088	56.673	1.567	12.951	0.909	34.967	0.271	5.5	7.5	584.2
3U	A	1	99.1	9.2	8.24	235	59.3	108.0	-13.924	-99.819	0.126	83.322	1.270	9.681	1.279	41.610	NA	4.7	6.6	546.3
3U	M	1	99.8	6.2	7.70	261	25.2	108.0	-13.971	-100.168	0.356	95.493	1.450	9.897	1.253	44.605	0.283	6.0	11.1	566.1
3D	A	1	99.9	8.8	8.16	220	61.5	126.0	-13.967	-100.173	0.103	79.744	1.235	8.887	1.240	40.081	0.269	6.3	5.6	540.3
3D	M	1	100.5	5.0	7.70	247	25.7	111.0	-13.932	-100.222	0.111	94.744	1.225	10.138	1.185	45.635	0.284	7.1	12.6	572.8
3T	A	1	98.5	10.6	8.11	113	2.2	198.0	-14.138	-102.546	0.091	35.554	1.097	7.151	0.418	25.680	0.193	4.0	8.5	556.6
3T	M	1	99.4	6.6	7.56	113	1.5	166.0	-14.229	-103.136	0.139	51.199	1.170	7.813	0.471	30.428	0.221	5.1	9.4	627.5
3Dp	A	1	99.6	8.2	8.17	226	69.1	123.0	-13.931	-100.051	0.192	57.941	1.185	11.508	0.552	35.950	0.283	4.7	13.6	538.2
3Dp	M	1	100.0	4.2	7.69	258	29.3	123.0	-13.959	-100.153	0.117	50.840	1.095	11.118	0.523	33.422	0.297	2.6	8.4	574.3
2U	A	1	92.6	9.9	8.14	237	25.0	143.0	-13.792	-99.420	0.127	89.514	1.298	9.709	1.466	44.253	0.264	4.8	8.9	552.8
2U	M	1	96.4	4.4	7.70	257	22.1	113.0	-13.952	-100.290	1.054	92.806	1.984	10.046	1.311	45.208	0.270	4.4	8.4	601.9
2D	A	1	93.6	10.0	8.14	235	24.6	116.0	-13.871	-99.552	0.102	100.868	1.215	10.185	1.594	48.693	0.325	4.3	10.6	551.3
2D	M	1	97.2	4.4	7.74	258	29.4	111.0	-13.935	-100.129	0.310	126.478	1.334	11.968	1.491	55.660	0.350	5.1	15.4	592.4
2T	A	1	95.4	8.1	7.90	122	1.4	606.0	-13.545	-97.652	0.132	91.130	1.287	9.457	1.463	44.484	0.275	9.5	7.8	1105.2
2T	M	1	92.2	5.8	7.60	120	1.1	564.0	-13.601	-98.032	0.192	111.825	1.295	10.885	1.366	50.790	0.332	10.7	2.5	1111.4
2Dp	A	1	97.5	7.5	8.12	222	63.2	111.0	-13.948	-99.944	0.190	58.410	1.646	5.972	0.808	27.765	0.139	4.0	8.1	550.4
2Dp	M	1	97.2	4.4	7.70	255	25.0	111.0	-13.942	-100.171	0.152	64.857	1.575	6.557	0.916	30.627	0.170	4.3	10.0	599.4
1Dp	A	1	99.0	7.6	8.14	224	26.0	126.0	-13.923	-99.724	0.157	96.687	1.227	10.094	1.630	47.931	0.296	3.9	8.6	602.8
1Dp	M	1	97.7	8.0	7.72	248	25.1	138.0	-13.895	-99.661	0.442	107.519	1.367	10.639	1.344	47.732	0.329	4.9	8.6	650.8

Table S1: Measured / sampled physicochemical and nutrient data

Supplementary Figures

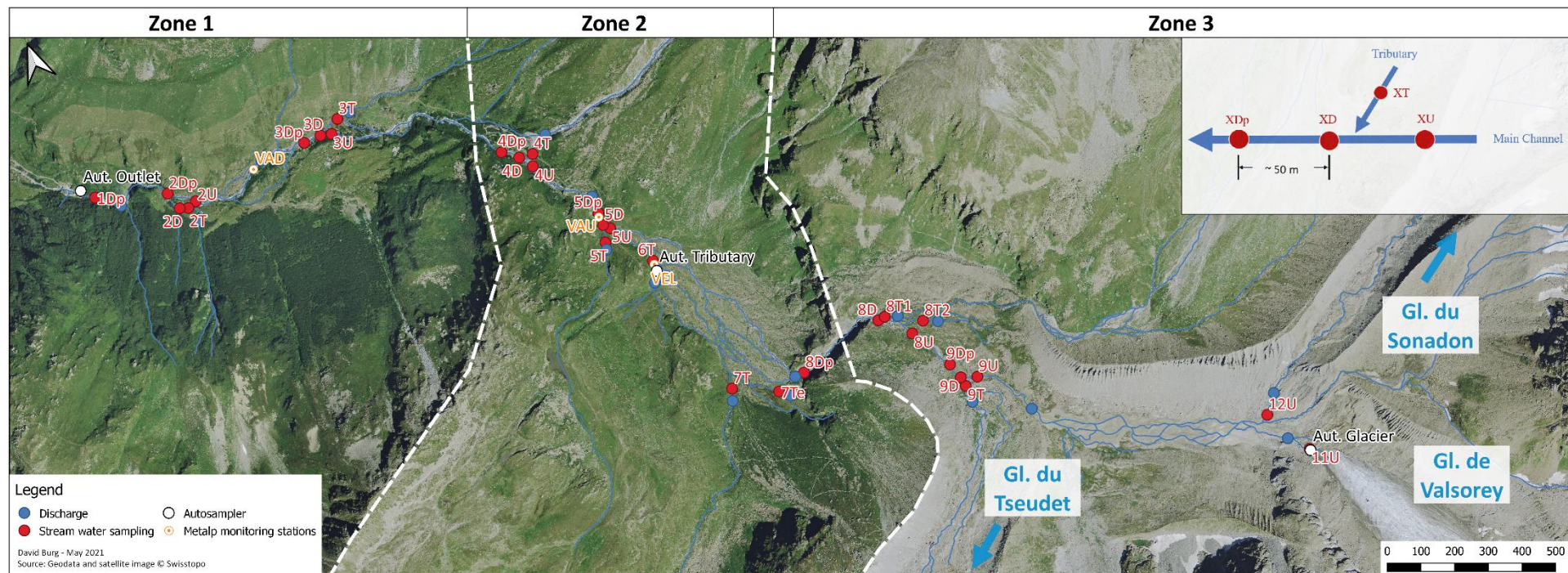


Figure S1: Map of Valsorey with sampling scheme, Metalp monitoring stations and locations of ISCO autosamplers. The zoom on the top right corner shows the general sampling scheme applied for sites 2, 3, 4, 5 and 9. The white dashed lines show the divisions of the catchment into three zones.

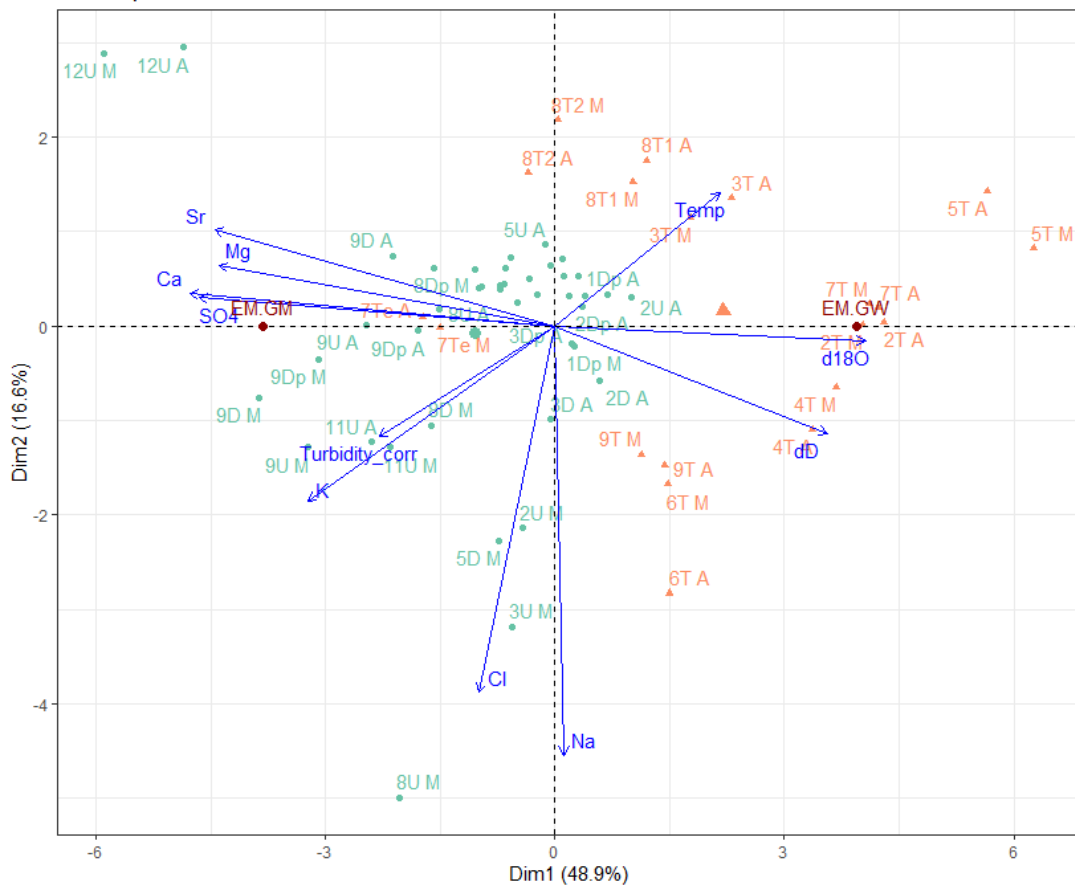
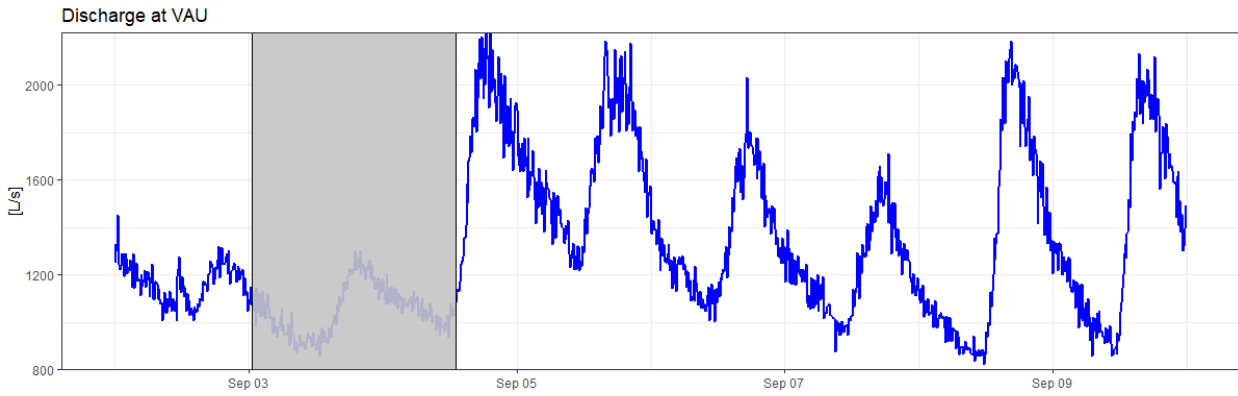
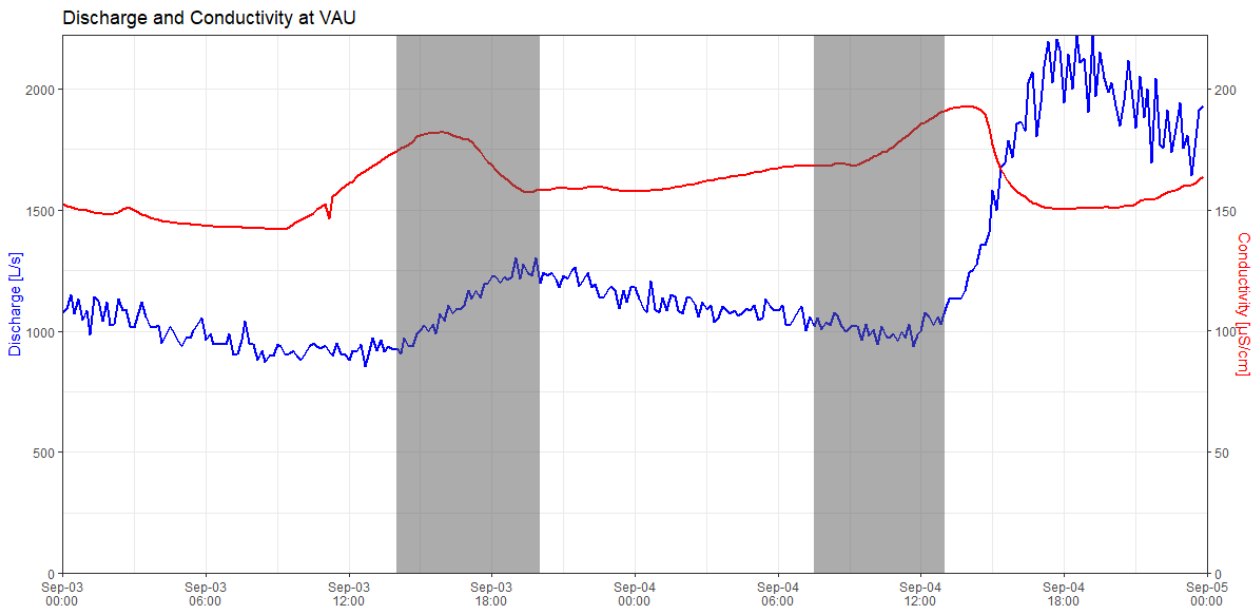


Figure S2: Principle Components Analysis used for the end-member mixing model. The percentages along the axes indicate the variance explained by the respective axes. PCA loadings are shown as blue arrows. PCA scores (sampling points) are coloured as belonging to the main channel (MC) or to a tributary (T). The location of the end-members used for the mixing model are shown as red dots on the x-axis (EM.GM denotes the glacier melt end member and EM.GW denotes the the groundwater end member). Sites are labeled with their site ID, followed by a letter: A=Afternoon, M=Morning; (Figure S1)

A



B



C

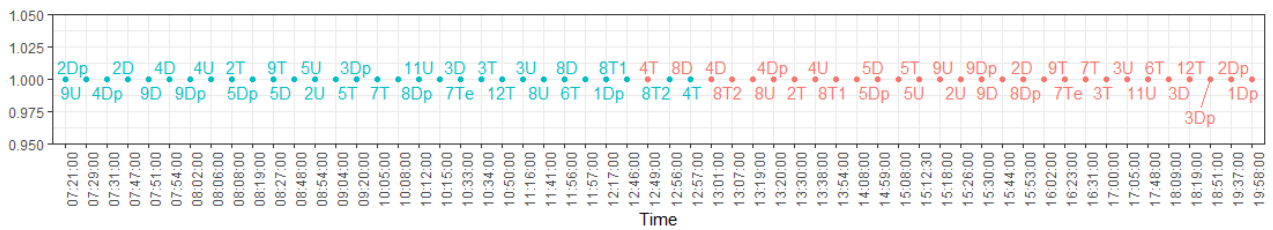


Figure S3: (A) Discharge at the VAU station of the Metalp monitoring program around the days of the sampling campaign. (B) Discharge and conductivity at the same station on the days of the sampling campaign. (C) Sampling times (as time of the day not continuous date and time) of the morning (blue) and afternoon (red) campaign.

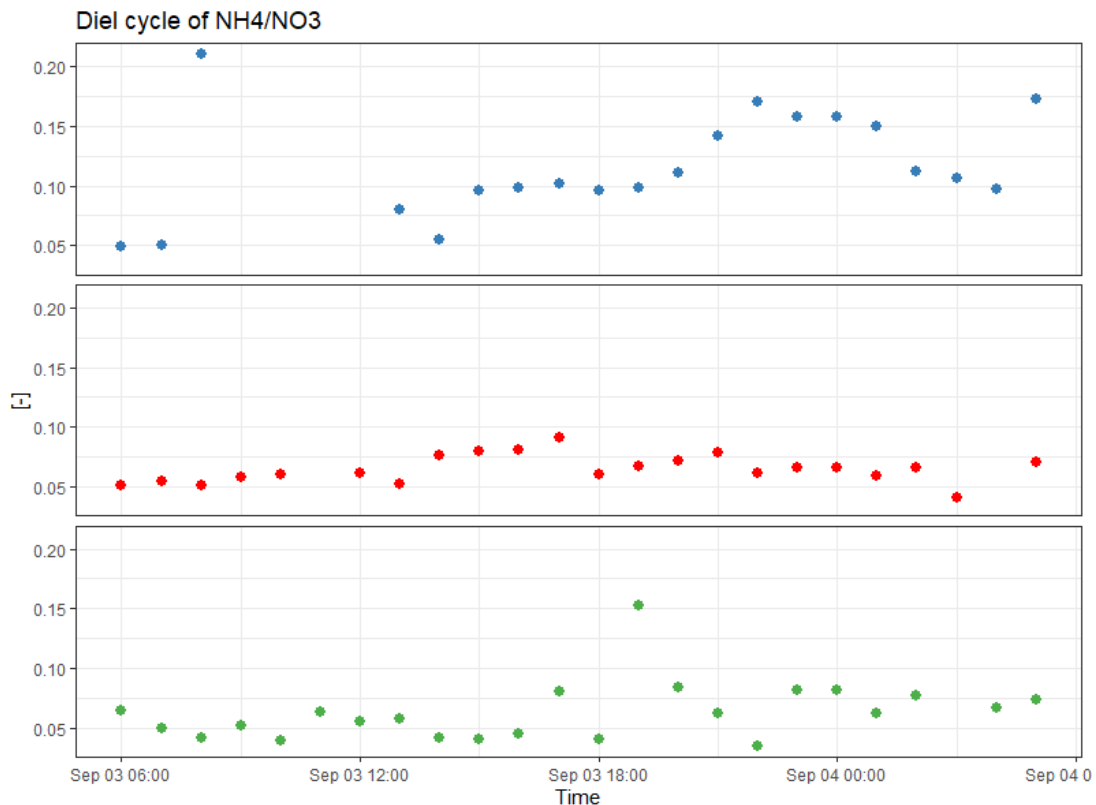


Figure S4: Diel cycle of NH_4/NO_3 ratio from ISCO autosamplers. Top panel: Valsorey glacier (11U), middle panel: tributary (6T), bottom panel: catchment outlet (1Dp).

Supplementary text

Uncertainties in mixing model and influence of sampling time on the results

Despite a careful choice of sampling design and thorough analysis of available discharge data for the definition of the sampling windows, logistical constraints in the realisation of the sampling have led to potential distortions in the afternoon to morning differences, despite the separation in the defined time frames. In particular, some of the samples taken at the beginning of the afternoon time frame may be very similar to their morning equivalents due to similar sampling times. An ideal sampling would have had all samples taken at the same time in the morning and in the afternoon.

The influence of the chosen sampling days should also be noted. A few days before the sampling, fresh snow had fallen on the higher regions of the catchment. By the time of the sampling, most of it had melted but the Valsorey glacier was still covered by a thin layer of snow. Since snow acts as an insulator, the glaciers probably melted less than expected thus diminishing the magnitude of their control on stream nutrient dynamics.

The mixing model approach leading to estimated fractions of glacier melt allows to eliminate sampling times. However, this approach is also affected by uncertainties. The first component of the PCA used in the mixing model explains 48.9% of the variance in the dataset. However, since this axis may be interpreted as a proxy of altitude, the global repartition of the sites in the space of principle components is meaningful. The choice of end members is also a source of uncertainty, but the approach of having averaged different glacier-fed streams and tributaries respectively strengthens the position of the end members on the PCA axis.