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Title: Topography and Land Use Modulate Hydrological and Nutrient Export Dynamics in Andean Streams

Short Title: Hydrology and Nutrient exports in Andean streams

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ABSTRACT

Waterways act as integrators of ecosystems, their dynamics driven by multiple environmental factors and scales. To elucidate factors affecting hydrological and nutrient dynamics in Andean streams, we characterized two adjacent North Patagonian streams with contrasting drainage basins: Casa de Piedra (CP), originating in a small mountain lake and running through a pristine landscape, and Gutiérrez (G), originating in a large piedmont lake and running through an anthropized landscape. The drainage basins share both temperature and precipitation regimes; however, the streams presented contrasting hydrological dynamics and nutrient export values. CP had higher discharge flashiness with shorter response delays to precipitation, while G showed more stable hydrograms, a difference explained by buffering from a large upstream lake in G's basin. Streams showed differences in the quality and timing of coarse particulate organic matter export and basal export levels of phosphorus and nitrogen that could be explained by human activities affecting G but not CP. Moreover, nitrogen:phosphorus ratio indicates a possible shift to phosphorus as the limiting nutrient in the future in G drainage basin. In summary, our results show that even under a common climatic regime, dynamics of adjacent basins can be strongly driven by topographic and land use factors.

INTRODUCTION:

River ecosystems have traditionally been studied as isolated entities; however, over time it has become clear that they are deeply intertwined with their surroundings (Likens 1985). Climate, topography, geology and land cover are environmental factors that control spatial patterns in these ecosystems through often hierarchical influence (Snelder & Biggs 2002). In other words, a river is the product of its landscape (Wiens 2002) and thus riverine hydrological, chemical and biological processes should be studied in relation to the river's overall drainage basin (Hynes 1975; Vannote et al. 1980).

Regional climate and drainage basin topography are factors acting at a macro and meso spatial scales upon the river ecosystem, strongly driving hydrological and chemical dynamics (Snelder & Biggs 2002). Climate directly drives the hydrological cycle, determining stream discharge, a key ecosystem variable. Discharge is fed by rain, snowmelt and groundwater, the relative importance of these factors varying over time and space (Brown et al. 2003). After a rain episode, surface and sub-surface run-off are favored at mountainous landscapes, while water infiltration and evapotranspiration are favored at highly vegetated lowlands with permeable soils. Snowfall at high altitudes contributes to formation of a snowpack, which will store water until the melt period, when this water flows down into a stream (Bailey 1995). Lakes are also topographic features of a drainage basin that can attenuate run-off response and sediment transport (Snelder & Biggs 2002). Thus, headwater lakes influence directly the hydrograph and sediment dynamic of downstream fluvial ecosystems (Gordon et al. 2004). These hydrographs tend to be stable over time, furthermore, considering lakes as sediment and nutrient traps, low values of nutrient concentration and export could be expected in these streams (Parker et al. 2009).

At a lower spatial scale, drainage basin traits also affect fluvial dynamics, since nutrients and contaminants generated at the basin eventually reach the river ecosystem (Allan 2004; Dodds & Smith 2016). Non-point source pollution, associated with changing land use patterns and practices, has resulted in increased impacts on water bodies (Jordan et al. 1997; Carpenter et al. 1998). For example, growth of urban areas favors nutrient export (Howarth et al. 1996; Meyer et al. 2005; Walsh et al. 2005). Moreover, direct dumping of sewage water to a stream greatly increases nutrient load (Pieterse et al. 2003) and can also change nutrient stoichiometry (Merseburger et al. 2005). Thus, increases of nutrient load leading to eutrophication of running waters and carbon dynamics largely depend on the drainage basin state.

In Northern Patagonia, climate and topography are largely determined by the Andes mountain range (Paruelo et al. 1998). According to the updated world map of the Köppen-Geiger climate classification, Northern

Patagonia is characterized by a temperate climate with warm and dry summers (Peel et al. 2007). The Andes represent an important barrier for humid air masses brought from the Pacific Ocean by westerly winds. Most of the humidity in these maritime air masses precipitates on the west side of the Andes as they are blown to higher, colder altitudes across the mountain range. Upon crossing the Andes, the air descends along their east side and becomes hotter and drier through adiabatic warming. East of the Andes, the amount of rainfall follows a steep west-east gradient: annual precipitation drops from 3500 mm to 700 mm in less than 60 km. Moreover, the precipitation regime shows marked seasonality, with most rain falling during fall and winter (Paruelo et al. 1998). Thus, in this mountain region, the hydrological regime of fluvial ecosystems can be divided into three contrasting periods (Sosnovsky et al. 2019): 1) a storm period, in which stream discharge variability and water turbidity are high due to high run-off and the interaction between land and river ecosystems; 2) a snowmelt period, with highest stream discharge and electrical conductivity (EC) dilution values; and 3) a dry period, with overall low stream discharge values and stronger influx from groundwater.

North Patagonian drainage basins along the East side of the Andes are in a relatively pristine state. In this region, many river systems originate from high-altitude wetlands and small lakes, or large piedmont lakes. Human population density is low, and native forest occupies the western, most humid zone while steppe vegetation occupies the eastern zone (Mermoz & Martín 1987). Forests are dominated by the genus *Nothofagus* (southern beeches) and Andean cypress species *Austrocedrus chilensis*, but other deciduous and evergreen species of high ecological and commercial value are present (Veblen et al. 1996). As in other South American temperate forests, N deposition is remarkably low (Holland et al. 1999), and vegetation is limited mainly by N (Diehl et al. 2003). Soils are classified as Andisols, which are characterized by high capacity to stabilize organic matter, store water and retain phosphorous (Satti et al. 2003). They also have a high pH buffering capacity. Work carried out in these drainage basins has revealed the oligotrophic character of the fluvial ecosystems (Pedrozo et al. 1993). Diverse authors have studied anthropic (Miserendino et al. 2016) and natural (Lallement et al. 2016; Williams Subiza & Brand 2018) elements that have affected Andean drainage basins, and consequently, their fluvial ecosystems. Some of these effects are sustained on chemical and biological structure over time (Carrillo et al. 2018). Recent research has revealed the dynamics of organic matter, which is intimately associated with the stream-basin interaction (García et al. 2015b; Díaz Villanueva et al. 2016; García et al. 2018). Nevertheless, studies focusing on stream discharge (Masiokas et al. 2008; Barros & Camilloni 2016; Sosnovsky et al. 2019) and, nutrient load or export (Oyarzún et al. 1998; Oyarzún et al. 2004; Temporetti 2006) are scarce; despite the hydrological, ecological and human importance of these variables. Even scarcer are studies where natural

processes and undisturbed nutrient cycling can be assessed in pristine ecosystems (Hedin et al. 1995) like the ones can be found in North Patagonian region.

The main hypothesis of our study is that climate is the principal driver of stream ecosystems dynamics, which are in turn modulated by topography and land use. As a consequence, we expect precipitation, air temperature and stream discharge to be intimately connected. In turn, adjacent drainage basins with contrasting topography and land use should present differences in their hydrological, physical and chemical dynamics. To test this hypothesis, we selected two streams located in adjacent yet contrasting drainage basins: Casa de Piedra (CP) and Gutiérrez (G). CP drainage basin is pristine, and the stream originates in a high-mountain lake. G drainage basin suffers from significant anthropization, and the stream originates from a large piedmont lake. On one hand, we expect to find buffered hydrological and chemical dynamics in G, relative to CP. On the other, higher anthropization of G´s basin could impact the stream ecosystem, potentially causing elevated or unpredictable variability in discharge regime along with increase nutrient concentration and export. Our first goal is to compare discharge variability of CP and G, and study how discharge relates to climatic variables (basin precipitation and air temperature). Our second goal is to determine the trophic state of these two streams, by measuring basal concentration, export and stoichiometry of nitrogen (TN: total N) and phosphorous (TP: total P), and estimate basal export of coarse particulate organic matter (CPOM, organic matter > 1mm). Our third objective is to identify seasonal patterns of key physical and chemical variables.

MATERIALS Y METHODS

Study area

Research was conducted at the drainage basin of the streams Casa de Piedra (CP; 41° 07’ 30.11” S 71° 27’ 13.16”W) and Gutiérrez (G; 41° 09’ 36.18” S 71° 24’ 37.19”W), both located in Nahuel Huapi National Park, Rio Negro, Argentina (Fig. 1). These drainage basins are very different from each other, despite of their proximity (Table 1). CP’s basin covers 63 km^2 and the stream originates in lake Jakob, a small (0.15 km^2), ultra-oligotrophic (1-3 $\mu g\ l^{-1}$ TP), high altitude water body situated at 1550 m a.s.l. (García et al. 2015a). CP’s only perennial affluent is the Rucaco stream, which originates at a high-altitude wetland. CP flows 19.7 km through a steep V-shaped valley (average slope: 33.9 m km^{-1}) from most of its length. CP’s drainage basin is mostly pristine, with human activities restricted to hiking and infrequent camping; human population (less than 1000 inhabitants, 2010 National Census) is restricted to lowland areas. Forest below the tree line includes deciduous *Nothofagus pumilio* and evergreens *N. dombeyi* and *Austrocedrus chilensis*. In contrast, G’s drainage basin is

larger (160 km^2), and the stream originates in lake Gutiérrez, a deep (111 m maximum depth) and large (17 km^2) water body that occupies ~11% of the basin's area. The seasonal concentration of TP is 3.4 μg l^{-1} on average (Diaz et al. 2007). G's only perennial affluent is the Cascada stream, whose catchment covers 12.5 km^2 and includes a major summer and winter sports resort. G flows 9 km through a wide, gently sloped valley (5.9 m km^{-1}). Its riverbanks are extensively colonized by the exotic crack willow, *Salix fragilis*, and pass through a series of populated areas (approximately 4000 inhabitants, 2010 National Census) belonging to the city of San Carlos de Bariloche (approximately 108000 inhabitants, 2010 National Census). In addition, two trout farms with a total production of ~3 tons $year^{-1}$ use G's waters. In summary, CP's basin is largely free of impact from human activities, while G's basin is not.

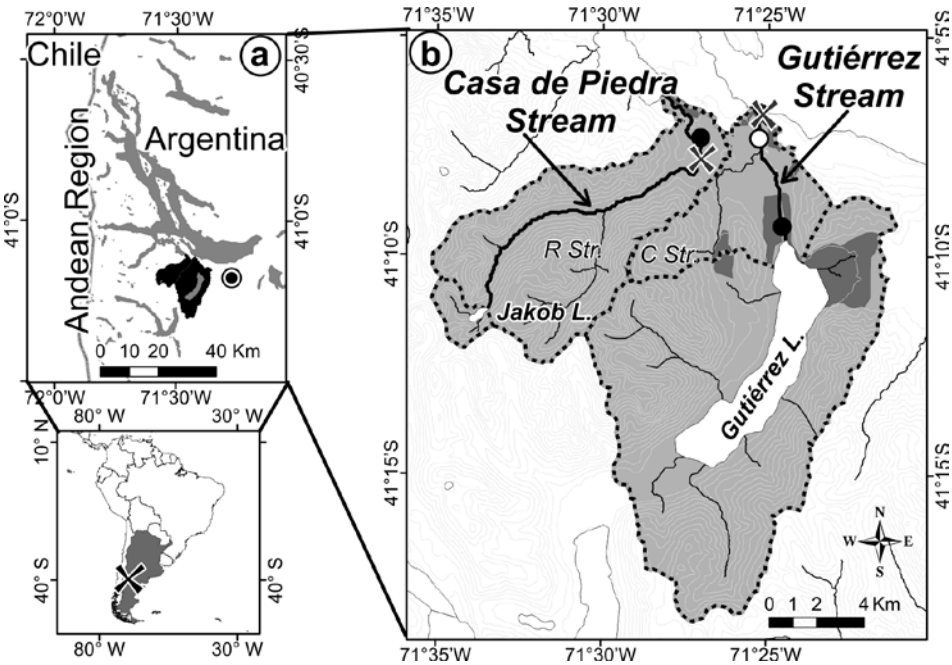

Fig. 1 a) Nahuel Huapi National Park; the study site is shaded in black. The city marker indicates San Carlos de Bariloche downtown. b) Study area, Casa de Piedra and Gutiérrez drainage basins, Jakob lake and Gutiérrez lake sub-catchments are also delimitated. Curves represent 100 m slope on the terrain. Populated zones are shown in grey, crosses indicate sampling sites, black circles indicate the Limnigraphic stations and white circle indicate the rain meter location. R Str. and C Str., Rucaco and Cascada streams (modified from Sosnovsky et al. 2019).

Data collection

The present study was carried out over a period of one year, from March 2013 to March 2014. Data on rainfall and discharge was kindly provided by the Rio Negro province's Water Department. Daily precipitation was recorded with a rain meter (Fig. 1), and did not differentiate between rain and snow. Discharge data were average daily records from limnigraphic stations. CP's limnigraphic station is located close to its mouth, while

G's station is located at its source (Fig. 1). Values of discharge at our G sampling site were estimated as discharge as measured at the station plus discharge for the Cascada stream, determined using the Drainage-Area Ratio method (Emerson et al. 2005); based on the specific daily values of discharge for the adjacent CP stream. Specific discharge (Q^{sp}) was defined as discharge per unit area. Daily average air temperature records were obtained from the National Weather Service.

	Casa de Piedra	Gutiérrez
Drainage area (km2)	63.9 (60.3)	160.4 (30.1)
Lake area (km2)	0.15	17.21
Native Forest (%)	60.2 (61.7)	61.1 (56.3)
Bare ground (%)	(27.7) 29.7	(9.5) 17.2
Exotic Forest (%)	(10.5) 9.9	10.8 (34.2)
Habitants [N]	< 1000 (< 1000)	4900 (4000)
Urban area [km2]	0.65 (0.65)	11.35 (5.08)

Table 1 Drainage basins characteristics. The values are expressed based on the entire area of the drainage basins, values in brackets exclude the sub-catchment area of the Jakob lake and Gutiérrez lake.

Baseline levels of nutrients and relevant physical and chemical variables were obtained from monthly sampling at both streams (Fig. 2). Water samples were taken to analyze total phosphorus (TP) and total nitrogen (TN) concentrations. Water turbidity was measured with a Velp turbidimeter. Temperature, electrical conductivity (EC) at 25 °C and pH were measured with an Oakton probe. Coarse particulate organic matter (CPOM) was sampled with 2 drift nets (1-mm, 20 X 20-cm opening at the mouth) that were staked in the streambed and left to collect material for intervals of 10 to 200 minutes, depending on the amount of CPOM present in the stream. During October, high and fast stream discharge prevented us from placing Surber sampler nets at G, so we performed linear interpolation for this value. Data were taken exclusively on days without precipitation.

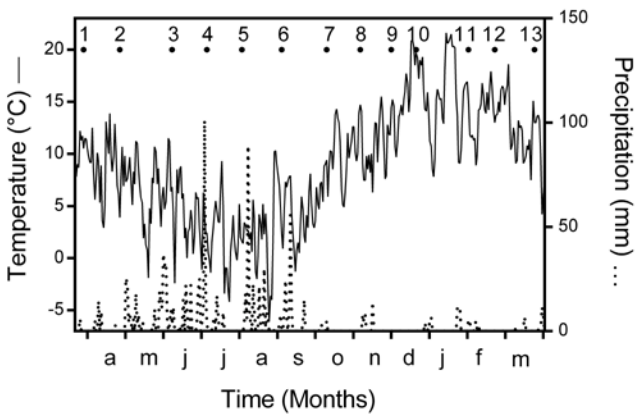

Fig. 2 Temperature and precipitation during the study period. Black dots and numbers indicate sampling dates

Data processing and analysis

Discharge

To understand the dynamics of discharge, we used an autocorrelation analysis (Mangin 1984) and calculated Richard- Baker (R-B) index (Baker et al. 2004). The autocorrelation analysis examines how a value depends on preceding values over a period of time. The correlations are computed for a given lag time *k* to obtain an autocorrelation coefficient *r(k)*. For example, the correlation between today´s and yesterday´s stream discharges would be a lag-1 autocorrelation coefficient, *r(1)*. The autocorrelation function is represented with a correlogram, where slope is determined by the response of the system to an event. If the event has only a short-term influence on the response of the discharge, the slope of the correlogram will decrease steeply. In contrast, if the system is influenced by an event for a long time, the slope of the correlogram will decrease slowly. Generally the length of the influence of an event is given by the "memory effect" which is according to Mangin (1984) the lag number *k* when *r(k)* reaches a value of 0.2. For this purpose, data on the average daily discharge were transformed to normality by the Box-Cox procedure as suggested by Peltier et al. (1998). The formula for autocorrelation is (Mangin 1984; Larocque et al. 1998):

$$r(k)\frac{C(k)}{C(O)}$$

with

$$C(k) = \frac{1}{n}\sum_{t=1}^{n-k}(x_t - \bar{x})\,(x_{t+k} - \bar{x})$$

Where *k* is the time lag and varies from 0 to *n*. According to Mangin (1984), *n* has to be taken as 1/3 of the whole dataset to avoid stability problems.

The annual variability in stream discharge (flashiness) was measured by the R-B index as follows:

$$R - B\ Index = \frac{\sum_{i=n}^{n}|q_i - q_{i-1}|}{\sum_{i=1}^{n} q_i}$$

The variable q is the mean daily discharge whereas n is the number of observations. This index measures oscillations in discharge relative to total discharge. Thus, it is a dimensionless measure ranging between 0 and 2 (Fongers et al. 2012). A value of 0 represents an absolutely constant discharge; increased R-B index values indicate increased flashiness of streamflow. As such, the index appears to provide a useful characterization of the way drainage basins process hydrological inputs into their streamflow outputs.

In addition, we studied the relationship between discharge, precipitation and temperature by cross-correlation analysis. This analysis is widely used to analyze the linear relationship between input and output signals in hydrology (Larocque et al. 1998). In this case, input signals were precipitation and temperature, and output signal was river discharge of CP and G streams. Cross-correlations are represented by a cross-correlogram. The maximum amplitude and the lag value of the cross-correlogram provide information on the delay, which indicates the time of the pulse transfer to the stream. According to Larocque *et al*. (1998) the formula for cross-correlation is:

$$r_{xy} = \frac{\mathrm{C}_{xy}\ (\mathrm{k})}{\sigma_x \sigma_y}$$

with

$$C_{xy}(k) = \frac{1}{n}\sum_{t=1}^{n-k}(x_t - \bar{x})\,(y_{t+k} - \bar{y})$$

Where σ_x and σ_y are the standard deviation of the two times series.

Physical and chemical analysis

We estimated concentration and export of nutrients (TN and TP) and CPOM. TN was analyzed through digestion and subsequent reduction in cadmium column (Grasshoff et al. 1983). TP was analyzed using acid digestion followed by evaluation of solubilized phosphorus as soluble reactive phosphorus (A.P.H.A. 2005). We estimated Ash Free Dry Weight of the CPOM using the Pozo et al. (2009) methodology. The annual export of TN, TP and CPOM were calculated by the following formula:

$$Nutrient\ export = \frac{[N]\ Q\ t}{A}$$

Where $[N]$ is nutrient concentration, Q is discharge, t is time and A is drainage basin area.

We performed a paired T-test to compare nutrient concentration and export between streams; to this end the data were transformed to comply with normality and homoscedasticity assumptions. Last, we performed a Principal Component Analysis (PCA) that included 12 variables: turbidity, temperature, EC, pH, discharge, TP, TN, TN TP^{-1}, CPOM, TP export, TN export and CPOM export. PCs were calculated based on standardized correlation matrix, using components with eigenvalues larger than 1. Number Cruncher (Hintze 1998) and InfoStat (Di Rienzo et al. 2016) where employed for statistical analysis, GraphPad Prism version 6.01 was employed for graphics editing.

RESULTS

Climate and hydrology of the region

Air temperature and precipitation in the study area agreed with a temperate climate. Air temperature was low between May and August and increased monotonically after September, reaching its highest values from December to February. Annual precipitation was 1164 mm and showed strong seasonality, with 80% falling between mid-May and mid-September. The first two (#1-2) and last three (#11-13) samples thus took place during a drier period; samples #3-6 were taken during the precipitation period; the remaining samples (#7-10) fell within the period of monotonic air temperature warming (Fig. 2). Thus, samples were evenly distributed across three climatically contrasting periods.

The flow regime was contrasting between the streams. CP had a lower annual average discharge value than G (Discharge $_{CP}$= 3.357 m^3/s; Discharge $_G$= 4.627 m^3/s; t =-7.4437; P < 0.0001; d.f. = 704), but its Q^{sp} was higher (Q^{sp}_{CP}= 0.051 m^3/s; Q^{sp}_G= 0.029 m^3/s; t=28.9156; P < 0.0001; d.f. = 487). CP presented the most extreme discharge values (Fig. 3a): the R-B index was 0.143 for CP, compared to 0.031 for G, indicating that the average day-to-day fluctuations of streamflow were 14.3 % and 3.1 %, respectively. Furthermore, CP showed a steep autocorrelation function with a memory effect at $k = 38$, while G revealed a more gently sloped function with a memory effect at $k = 61$ (Fig 3b). Thus, CP showed higher flashiness and lower memory (i.e., temporal persistence) than G.

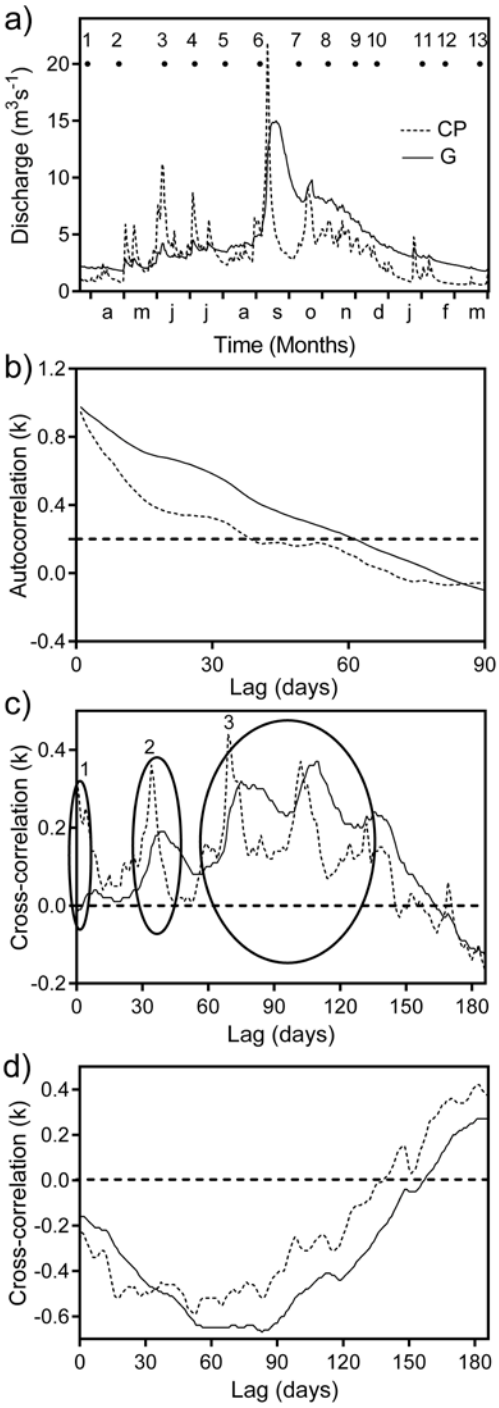

Fig. 3 a) Hydrographs of Casa de Piedra (CP) and Gutiérrez (G) streams, black dots and numbers indicate sampling dates. b) Autocorrelation functions and memory effects (r (k) = 0.2) of the discharge. c) Cross-correlations between discharge and precipitation, three different periods are shown, and d) cross-correlations between discharge and temperature.

Cross-correlation of discharge with precipitation and temperature showed opposing patterns. Discharge was positively correlated with precipitation, but negatively correlated with air temperature (Fig. 3c, d and Table S1). The discharge-precipitation correlogram shows three periods that coincide with peaks of the correlation function (Fig. 3c). Both streams show differences at each of these peaks: CP had higher correlation values (r_{max}) and lower lag times than G. Indeed, at CP the correlation reached its maximum the same day precipitation took place (lag = 0) during the first period, while r was not even significant for G at the time (Table S1). During the second period, correlation at CP reached an r_{max}=0.36 with a lag time of 34 days, while at G, correlation was lower (r_{max}=0.19) and the lag higher (lag = 40). The third, longest period presented a series of peaks and valleys, and lapsed from day 57 to day 110 after the precipitation event at CP and from day 62 to 142 at G. In contrast, the discharge-temperature correlogram did not show similar periods; cross-correlation was significant from day 0 to around day 90 for both streams (Fig. 3d, Table S1).

Physical and chemical characteristics of the streams studied

Although streams differed in the specific values, both had very low EC, turbidity, nutrient concentration and nutrient export (Table 2). G showed the highest TP and TN concentrations (Fig. 4a, c) and exports (Fig. 4b, d): CP exported 8.9 kg TP km^{-2} $year^{-1}$ and 59.0 kg TN km^{-2} $year^{-1}$, while G exported 11.7 kg TP km^{-2} $year^{-1}$ and 78.8 kg TN km^{-2} $year^{-1}$ (approximately 35 % more N). No significant differences in TN:TP average ratios were found (~15; Fig. 4e), although the median value of TN:TP was 11 for CP and 16 for G. As to the amount of CPOM exported, no significant difference between streams was found. There were differences, however, in the quality of exported material; native *N. pumilio* leaves dominated in CP, while introduced *S. fragilis* leaves dominated in G. The peaks of CPOM export also differed among streams: highest export at CP was found during June and July (samples #3-4), while at G this peak occurred earlier, in April (sample #2). In summary, the drainage basin showing more anthropic land uses also showed higher nutrient export, with most CPOM export represented by introduced tree species.

	Casa de Piedra	Gutiérrez
Temperature (°C)	7.8 (3.7-12.5)	10.6 (6.0-16.8)
Electrical Conductivity (µs cm^{-1})	43 (27-61)	74 (71-76)
Turbidity (NTU)	0.2 (0.0-0.8)	0.7 (0.0-2.0)
pH	7.8 (7.4-8.0)	7.9 (7.3-8.1)
Total Phosphorus (mg m^{-3})	5 (2-9)	14 (10-18)
Total Nitrogen (mg m^{-3})	29 (18-44)	94 (75-134)
TN TP^{-1} (molar)	15 (6-31)	15 (11-21)
Coarse Particulate Organic Matter (AFDW m^{-3})*10	0.46 (0.04-1.86)	0.91 (0.02-8.76)
Total Phosphorus export (kg km^{-2} y^{-1})	8.9 (1.7-26.4)	11.7 (3.8-22.6)
Total Nitrogen export (kg km^{-2} y^{-1})	59.0 (8.2-134.2)	78.8 (27.4-186.0)
Coarse Particulate Organic Matter export (kg km^{-2} y^{-1})	131.3 (1.3-778.2)	43.3 (1.5-320.2)

Table 2 Average values, maximum and minimum in brackets, of the physical and chemical variables in the streams (n=13, except for the Coarse particulate organic matter where n=12).

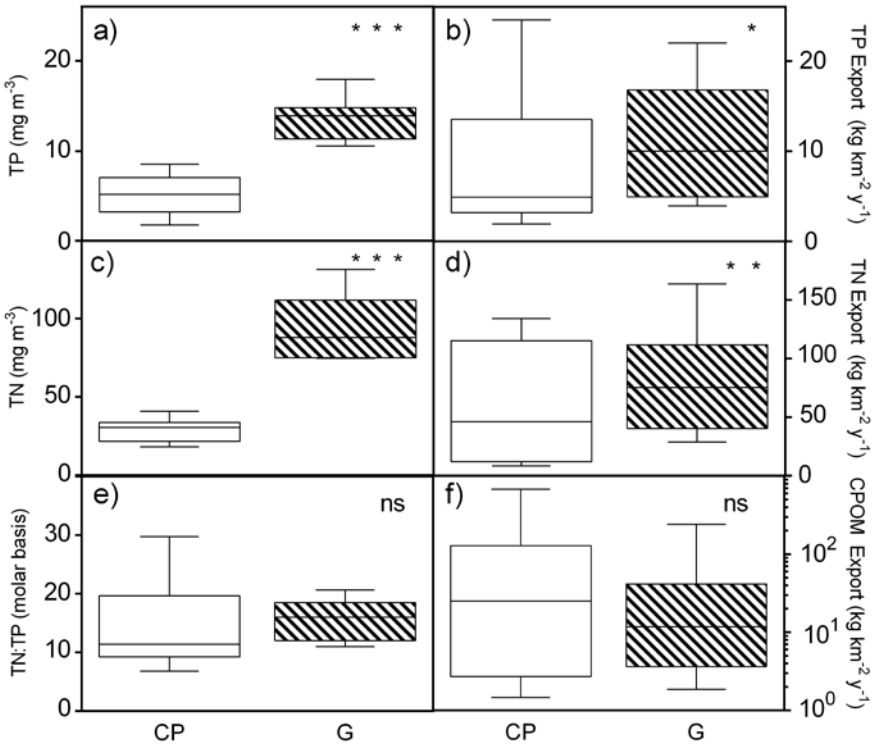

Fig. 4 Box plot showing annual differences in nutrient concentration, ratio and export in Casa de Piedra (CP) and Gutiérrez (G) streams (Paired T Test, * $P \leq 0.05$; * * $P \leq 0.01$; * ** $P \leq 0.001$; ns: not significant). f) The Y axis is in logarithmic scale. Total Phosphorus (TP), Total Nitrogen (TN) and Coarse Particulate Organic Matter (CPOM).

Our PCA determined three Principal Component, FI, FII and FIII that respectively explain 33%, 24% and 13% of the variance, accounting for 70% of the total variance (Table 3). FI was mainly related to discharge and nutrient export (TP_{exp} and TN_{exp}) (Fig. 5a). Positive FI values corresponded to samples with high discharge, high nutrient export and high turbidity. The FII was mainly related to the EC of the water, and to a lesser extent with water temperature and nutrient concentration (Fig. 5a). The FIII was mainly related to the TN:TP ratio, and to a lesser extent with CPOM variables.

Variable	First Factor (33%)	Second Factor (24%)	Third Factor (13%)
Temperature		0.31	
EC		0.47	
Turbidity	0.35		
Q	0.38		
TP	0.35	0.41	
TN	0.36	0.32	
TN TP^{-1}			0.55
CPOM			-0.47
TP_{exp}	0.42		
TN_{exp}	0.42		
$CPOM_{exp}$		-0.35	-0.55

Table 3 Principal Component Analysis on physical and chemical variables. Factors are a linear combination of the different variables. Percent of variance explained and factor loadings (> 0.30) are shown. Abbreviations are as in Figure 5.

Both streams are clearly discriminated by PCA ordering, highlighting seasonal differences in each stream (Fig. 5b). Besides separating samples from each stream, plotting FI versus FII shows that each stream is temporally heterogeneous, allowing clustering in 3 groups for CP (CP_A, CP_B and CP_C) and 2 for G (G_A and G_B) (Fig. 5b). CP_A had low discharge and export rate values and high temperatures, taking place at the warmest period (Fig. 2). CP_B had higher nutrient concentration and export values, matching the period with more abundant precipitation (Fig. 2). CP_C was mainly characterized by low EC, nutrient concentration and turbidity values, and coincides with the period of diminishing rainfall and monotonic air temperature warming (Fig. 2). G_A had similar characteristics to CP_A and spans the same period. The remaining samples fall within G_B. Thus, the values of physical and chemical variables sampled monthly through the year show that both streams have marked seasonal differences that follow precipitation and air temperature patterns.

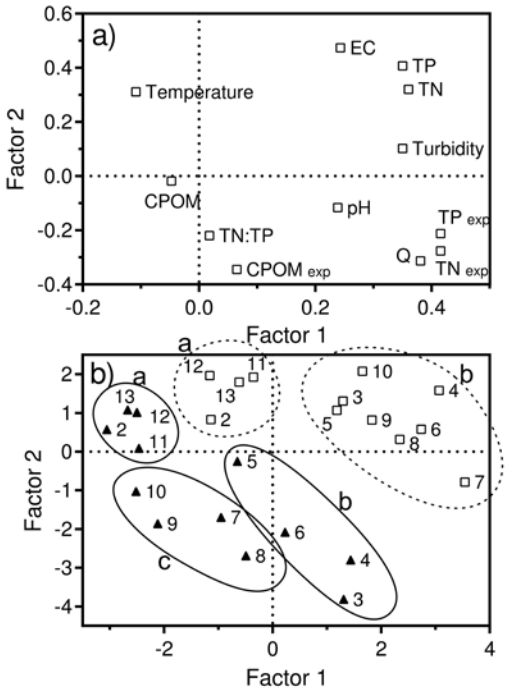

Fig 5 Principal Component Analysis (PCA) of physical and chemical variables in the study streams. a) The weight of variables in each of the axes is shown. b) First factorial plane of the PCA, Casa de Piedra sampling dates are represented by triangles and Gutiérrez ones are represented by rectangules, the numbers correspond to the sampling dates and they are grouped by climatic characteristics of the region (a, b and c). Electrical conductivity (EC), Discharge (Q), Total Phosphorus (TP), Total Nitrogen (TN), Coarse Particulate Organic Matter (CPOM), Export (exp).

DISCUSSION AND CONCLUSIONS

We surveyed discharge and nutrient dynamics in two adjacent North Patagonian streams with contrasting drainage basins. Precipitation had a direct influence on the magnitude of stream discharge at both streams, but the response time varied between them. CP stream was flashy, showed a tighter relation between precipitation at the basin and discharge response and stronger seasonality of physical and chemical parameter values. G stream, in contrast, showed a more buffered discharge response to precipitation and higher nutrient exports. In general, similarities seen between streams can be related to regional climate, while differences are better explained by contrasting topography and land use of the respective drainage basins.

Precipitation and temperature have opposite influence in river discharge in the Andean region (Masiokas et al. 2008). In this way, precipitation increased stream discharge of our study sites, while elevated air temperature periods produced the opposite effect. The different pathways taken by precipitated water to reach

the streams (run-off, groundwater and snowmelt) (Brown et al. 2003) and their relative importance are evidenced by the three periods found in the discharge-precipitation correlogram. Surface run-off was more relevant at CP, a stream that feeds from run-off from a basin characterized by steep slopes and the lack of buffering from a large upstream lake. In this stream, discharge increased drastically during the same day precipitation occurred, and the following days. Water that does not reach the stream immediately as run-off, infiltrates into the soil and moves to the stream as sub-surface run-off or groundwater; these pathways usually results in a delayed stream discharge response (Kalff 2002). This delay time was close to a month for both streams; this similarity suggests that both basins share the same subsurface geological traits, and thus that geology drives groundwater dynamics. The sub-surface run-off and groundwater pathways were also more relevant at CP, which showed a higher *r(max)* and shorter delay times. In colder regions, snow precipitation is stored during the winter months and released as snowmelt in spring and summer (Bailey 1995). This results in a delay time between precipitation and discharge response of about 2-4 months, as we found at both study sites during spring. Such discharge dynamics and its relationship with the fractions of precipitation fallen as either rain or snow match the storm and melt periods described at other mountainous regions (Ahearn et al. 2004).

The presence of a headwater lake in the drainage basin regulates the flow regime of a stream (Baker et al. 2004). This was made evident by the contrasting values of discharge autocorrelation and flashiness R-B indices between the streams in our study. The autocorrelation function fell sharply for CP but sloped more gently for G, showing a shorter memory effect (Mangin 1984) in CP, and agreeing with differences in annual values of the R-B index. Flashiness values seen at CP (R-B = 0.14) are similar to those found for streams at Austria (R-B = 0.18) and Slovakia (R-B = 0.15) that flow through basins with steep slopes and small area (Holko et al. 2011). In contrast, flashiness at G was much lower (R-B=0.03), and more akin the values found for streams with regulated flows at Indiana, USA (Baker et al. 2004). Thus, the difference in flashiness between the adjacent streams we studied is explained by the contrasting topography of their drainage basins, including the presence of a large lake in one but not the other.

Leaves of riparian trees are generally the largest component of allochthonous inputs to stream located in forested drainage basins and are often the major source of energy to heterotrophic organisms (Vannote et al. 1980; Webster et al. 1999)**.** In the case of Andean streams, *N. pumilio* leaves cover large areas of the waterway during autumn (Albariño et al. 2009). A substantial amount of these may be transported downstream by spates occurring from late autumn to winter and eventually reaches the lake (Modenutti et al. 2010). We observed no significant differences in the amount of CPOM exported by the two streams studied. However, we highlight the

fact that in stream CP the CPOM was mainly made up of native *N. pumilio* leaves, while in stream G introduced *S. fragilis* leaves dominated. This corresponds to the tree species present in the different catchments, and could explain the temporal difference between streams in the surge of CPOM; the peak in CPOM export occurred during June and July in stream CP, and during April in stream G. This supports the claim that afforestation or invasion of exotic plants with different phenology, chemical and physical characteristics to those of the native riparian species changes the timing, quantity and quality of leaf litter standing stock in streams (Naiman et al. 2005).

Streams in the north Patagonian region are oligotrophic (Pedrozo et al. 1993; García et al. 2015b). The concentration and the annual export rate of the nutrients from CP stream reflected this characteristic. Values of N and P concentrations were lower to those measured in a forested nearby sub-catchment (TN = 110.6 µg l^{-1} and TP = 9.6 µg l^{-1}) while they were much smaller than those found in a burned sub-catchment of this region (TN = 675.1 µg l^{-1} and TP = 12.0 µg l^{-1}) (Temporetti 2006). Values of N export were lower to those measured in areas of low anthropogenic impact in Patagonia (average TN export = 100 kg km^{-2} $year^{-1}$) (Little et al. 2008), and values of P export were between the lowest measured in South America (TP export range from 4 to 450 kg TP km^{-2} $year^{-1}$) (Álvarez-Cobelas & Angeler 2007). These results indicate that nutrient export in CP river ecosystem is among the lowest measured for any basin worldwide (Álvarez-Cobelas et al. 2008; Álvarez-Cobelas et al. 2009). However, it should be taken into account that we have estimated basal nutrient export rates because we measured them in days without precipitation, when their export tend to be low (Tate & Singer 2013). In any case, it is interesting to note that these rates were higher for stream G than for CP, even though the opposite result could have been expected, given that headwater lakes act as nutrient and sediment traps (Parker et al. 2009). The higher nutrient concentration seen at G is thus not explained by natural causes, but by the effects of land use in its drainage basin, namely the presence of human settlements and trout farms.

Increases in eutrophication levels of river ecosystems is due to both point and diffuse sources (Carpenter et al. 1998). While we did not formally weigh the relative impacts of fish farming and urbanization, we suspect that a growing residential settlement of the Gutiérrez stream drainage basin, often times without adequate wastewater treating infrastructure, is expected to have a larger impact than the detritus from fish farms producing ~3 tons of fish per year. This is partially supported by nutrient measurements at G stream during the low water period where dissolved inorganic nitrogen export (DIN_{exp}) was measured downstream the larger fish farm (DIN_{exp} = 7 kg km^{-2} $year^{-1}$) and at its mouth (DIN_{exp} = 108 kg km^{-2} $year^{-1}$) (Sosnovsky, unpublished results). Moreover, the additional nutrient sources of fish food and feces from salmonid production decrease the TN:TP

ratio of the water column in Patagonia reservoirs (Diaz et al. 2001), a fact we did not observe in G stream. However, a more detailed spatial study in G drainage basin aimed to determine the sources and sinks of total and dissolved nutrients associated to eutrophication processes is still necessary.

The molecular N:P ratio is said to distinguish nitrogen-limited systems from those constrained by phosphorus (Rhee & Gotham 1980). Kahlert (1998), in a review of the literature, found that the optimal N:P ratio of freshwater benthic algae was 18:1 (molar), which deviates from the phytoplankton optimal stoichiometric N:P ratio of 16:1 (Redfield ratio) (Goldman et al. 1979). CP and G streams had an arithmetic mean N:P molar ratio close to 15, which would indicate nitrogen deficit in these ecosystems, similar to what has been observed in other ecosystems of Northern Patagonia, either forests (Satti et al. 2003) or lakes (Diaz et al. 2007). However, considering that median values of N:P were 11 for CP and 16 for G, it becomes evident that nitrogen limitation is being lifted at G, most likely due to wastewater leaching from human settlements. An increase in the N load is expected to result in increased eutrophication of the G stream and downstream water bodies. Thus, it would be advisable to build adequate wastewater treatment plants to avoid driving these, up until now, low impact drainage basins towards ecosystem eutrophication. Our findings at the drainage basin level are in line with observations at the global scale suggesting human actions generate a clear unbalance favoring N over P (Peñuelas et al. 2013).

By studying two Andean streams located at adjacent, yet contrasting drainage basins, we were able to investigate the influence of environmental factors acting at different spatial scales over these freshwater ecosystems. At a regional scale, climate determined seasonality of water flow for both streams. At a landscape scale, we found that the presence of a large, deep lake buffered the hydrological dynamic of its effluent stream. At a lower spatial scale, we found that more intense human impact at G's drainage basin correlated with higher nutrient export rates by the stream. Considering the strong demographic pressure at G's drainage basin, there is a high risk of change in N:P stoichiometry and ecosystem eutrophication. Gutiérrez basin situation thus shows a stark contrast to Casa de Piedra basin, which instead has the hydrological, physical and chemical dynamics of a pristine drainage basin characteristics of Andean streams originating at high altitude wetlands and small lakes (Sosnovsky et al. 2019). Besides geomorphology, the main differences between both basins are land use policies: CP's basin is mostly within protected areas, while most of G's lower basin is within the limits of San Carlos de Bariloche city and subject to several, potentially high impact uses, like residential neighborhoods, winter sports and fish farming, among others. Local and global environmental problems are currently burning issues in stream ecosystem processes and will be even more so in the future. Considering that lakes and streams are sentinels and

integrators of environmental change in the surrounding terrestrial landscape (Williamson et al. 2008), it is really important to monitor the key variables of these aquatic ecosystems (Lovett et al. 2007) and emphasize the preservation and restoration of their drainage basins.

Author contributions

Alejandro Sosnovsky performed the study conception and design. All authors contributed to the material preparation, data collection and analysis. The first draft was written by Sosnovsky, Alejandro and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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