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Climate-driven terrestrial inputs in ultraoligotrophic mountain streams of Andean Patagonia revealed through chromophoric and fluorescent dissolved organic matter

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HIGHLIGHTS

- Allochthonous inputs in Patagonian streams were surveyed for 30 months.
- Particulate materials, dissolved organic carbon and nutrients increased with runoff.
- Allochthonous carbon contributed through runoff dominates the streams' DOM
- DOM analyses converge to point out to the catchment carbon contribution.
- DOM quality reflects different breakdown stages of allochthonous DOM.

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ABSTRACT

Fluvial networks transport a substantial fraction of the terrestrial production, contributing to the global carbon cycle and being shaped by hydrologic, natural and anthropogenic factors. In this investigation, four Andean Patagonian oligotrophic streams connecting a forested catchment (~125 km^2) and draining to a double-basin large and deep lake (Lake Moreno complex, Northwestern Patagonia), were surveyed to analyze the dynamics of the allochthonous subsidy. The results of a 30 month survey showed that the catchment supplies nutrients and dissolved organic matter (DOM) to the streams. The eruption of the Puyehue–Cordón Caulle at the beginning of the study overlapped with seasonal precipitation events. The largest terrestrial input was timed with precipitation which increased particulate materials, nutrients and DOM through enhanced runoff. Baseline suspended solids and nutrients were very low in all the streams (suspended solids: ~1 mg/L; total nitrogen: ~0.02 mg/L; total phosphorus: ~5 μg/L), increasing several fold with runoff. Baseline dissolved organic carbon concentrations (DOC) ranged between 0.15 and 1 mg/L peaking up to three-fold. Chromophoric and fluorescent analyses characterized the DOM as of large molecular weight and high aromaticity. Parallel factor modeling (PARAFAC) of DOM fluorescence matrices revealed three components of terrestrial origin, with certain degree of microbial processing: C1 and C2 (terrestrial humic-like compounds) and C3 (protein-like and pigment derived compounds). Seasonal changes in MOD quality represent different breakdown stages of the allochthonous DOM. Our survey allowed us to record and discuss the effects of the Puyehue–Cordón Caulle eruption, showing that due to the high slopes, high current and discharge of the streams the volcanic material was rapidly exported to the Moreno Lake complex. Overall, this survey underscores the magnitude and timing of the allochthonous input revealing the terrestrial subsidy to food webs in Patagonian freshwaters, which are among the most oligotrophic systems of the world.

1. Introduction

A considerable fraction of the primary production of the terrestrial environment is transported by fluvial networks contributing significantly to the global carbon cycle (Battin et al., 2009; Fasching et al., 2014). The delivery of terrestrial dissolved organic matter (DOM) into inland water is driven by several natural (i.e. climate, landscape, etc.) and anthropogenic (i.e. land use) factors, and is controlled by hydrologic processes (Ågren et al., 2008; Laudon et al., 2011; McElmurry et al., 2013). As a consequence of global climate change and human impact on natural landscapes, the flux of terrestrial DOM into inland waters is rising, causing the browning of freshwater networks in some regions of the world (Fasching et al., 2014). The terrestrial DOM subsidy has

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an important role in catchment carbon budgets influencing the biogeochemistry and ecology of surface waters (Cole et al., 2007; Nilsson et al., 2008). The inputs of allochthonous colored organic matter (CDOM) into the watersheds are tied to climate variables and may influence environmental aspects such as light penetration, primary production, and microbial communities, with far reaching effects in aquatic food webs (Jansson et al., 2007; Jaffé et al., 2008; Mladenov et al., 2011; Fasching et al., 2014).

DOM is composed of different organic substances with particular reactivities and ecological functions (Jaffé et al., 2008). In particular, dissolved organic carbon (DOC) exerts control on the acid–base chemistry of soils and surface waters (Hruška et al., 2003) and affects metal export and speciation (Ravichandran, 2004; Aiken, 2014). The properties of DOM are diverse and depend on its source and diagenetic state (Benner, 2003). DOM quantity and quality are in turn controlled by a variety of processes, biological (e.g. primary production and decomposition), chemical (e.g. photodegradation and redox reactions) and physical (e.g. hydrology) (McKnight et al., 2001; Findlay and Sinsabaugh, 2003; Jaffé et al., 2008; Fellman et al., 2009; Spencer et al., 2009). Qualitative assessments of bulk DOM include molecular weight, aromaticity, optical properties, elemental composition and proportion of humic substances (Hessen and Tranvik, 1998; Helms et al., 2008; Ishii and Boyer, 2012). Thus, monitoring the DOM dynamics provides substantial information about ecosystemic linkages and functioning over space and time (Larsen et al., 2010; Laudon et al., 2011; McElmurry et al., 2013; Fasching et al., 2014).

In running water, DOM is greatly influenced by the characteristics and processes of the watershed, particularly the regional climate (rainfall and temperature), the vegetation, the permafrost and wetland coverage as well as the channel slope and the discharge (Jaffé et al., 2008; Laudon et al., 2011; McElmurry et al., 2013; Fasching et al., 2014). In particular, in headwater catchments stream DOM is derived primarily from allochthonous sources such as ground and/or soil water, riparian zones and overland flow (Brooks et al., 1999; Hood et al., 2005). The majority of the annual DOC flux from the catchment to the fluvial network is contributed by the runoff (Boyer et al., 1997; Baker et al., 2000; Finlay et al., 2006).

The headwaters of the Atlantic and Pacific basins extending on both sides of the Andes in Northern Patagonia are born above the treeline in the high cordillera, draining mountain lakes and/or receiving directly transient streams originated in the snowpack. These systems cross barren or poorly developed soils above the timberline and areas lower in the catchment which are covered by endemic *Nothofagus* forests (Paruelo et al., 1998a) to finally reach large and deep piedmont lakes (Queimaliños et al., 2012; Garcia et al., 2015). Andean Patagonian catchments comprise some of the most unproductive freshwater systems of the world including mountain lakes and streams. Piedmont lakes and large rivers are characterized by limiting nutrient levels (Pedrozo et al., 1993), extremely low DOC concentrations (<1 mg/L) and challenging underwater UV levels (Morris et al., 1995). These factors act concomitantly as strong driving forces for ecosystemic processes (Marinone et al., 2006; Mladenov et al., 2011; Queimaliños et al., 2012). For example, the harsh underwater light climate of Andean Patagonian freshwaters boosts photochemical reactions, thus influencing biogeochemical processes and certainly inhibiting the occurrence and production of aquatic organisms (Pérez et al., 2002, 2007; Marinone et al., 2006).

The analysis of DOM in Andean Patagonian freshwater ecosystems has focused on estimating directly or indirectly the DOC concentrations and its influence on underwater light climate of lakes (Morris et al., 1995; Pérez et al., 2002, 2007, 2013). Mountain aquatic systems of Patagonia are apparently not affected by atmospheric inputs of nutrients and DOM (Mladenov et al., 2011), being the forested catchment the main source of allochthonous particulate carbon (Albariño and Díaz Villanueva, 2006) and the precipitation and runoff the vehicle to the fluvial network (Albariño et al., 2009; Queimaliños et al., 2012).

Forecasts for this region include shifts in precipitation and rising temperatures (Masiokas et al., 2008; Villalba et al., 2012), variables affecting the magnitude and timing of the allochthonous contribution to local aquatic systems (Bastidas Navarro and Modenutti, 2012; Queimaliños et al., 2012). In addition, the increasing levels of UV radiation in the region are expected to enhance the photochemical reactions leading to changes in the availability and reactivity of DOM, and probably cascading into other trophic compartments in aquatic systems (Häder et al., 2007, 2011).

The dynamics of Andean catchments is shaped by the frequent disturbances generated by volcanism affecting at a regional scale along with mass movements, avalanches and fires acting at local and micro-scale (Daniels and Veblen, 2003; Daga et al., 2008, 2014). Nahuel Huapi National Park (NHNP, North Patagonia, Argentina) is located in the Southern Volcanic Zone (SVZ) of the Andes, under the influence of several active volcanoes, with high eruption frequency recorded in historical descriptions since the 18th century (Daga et al., 2008). Three main volcanic sources have been determined in sediment cores of different lakes of the NHNP, Puyehue–Cordón Caulle complex (PCC) and the volcanoes Chaitén and Calbuco. On 4th June 2011 the volcanic complex PCC (40°30′S, 72°12′W; 2236 m a.s.l) erupted, expelling a column (height: 11–15 km, width: 5 km) of pumice, ash and gases to the atmosphere lasting until March 2012 (Daga et al., 2014). The eruption dispersed volcanic products to the southeast impacting NHNP as well as the Patagonian steppe, reached the Atlantic Ocean in one day, circling the globe few days later (Cardona et al., 2012; Klüser et al., 2013). The eruption of the PCC deposited around 950 million tons of ash on Argentine Patagonia, creating a layer of volcanic material of varying thickness and particle size, depending on the distance from the source (Chaneton et al., 2014). Volcanism in Patagonia is known to determine regionally soil properties (Diehl et al., 2003), and to affect terrestrial and aquatic biota inducing changes at community level and causing the disruption of ecological interactions (Modenutti et al., 2013; Chaneton et al., 2014; Elser et al., 2015). In streams close to PCC, the pumice and ash cumulated on the riparian vegetation and streambeds, changing water quality parameters and communities, while in lakes of the area there was an increase in total suspended solids, light extinction, phosphorus concentration and phytoplankton biomass (Modenutti et al., 2013; Balseiro et al., 2014).

This investigation aims to analyze the magnitude, quality and the timing of the allochthonous subsidy in four streams that drain a pristine forested catchment in Northwestern Patagonia. In particular, we focused on the temporal dynamics and the hydrological and biochemical controls of DOM in four Andean streams (Casa de Piedra, Goye, López and De la Virgen), draining a forested catchment of ~125 km^2 towards the double-basin, deep, ultraoligotrophic Lake Moreno (NHNP, Patagonia, Argentina). For this purpose, we sampled the four streams for 30 months, recorded the discharge and physico-chemical parameters, and performed laboratory analyses to determine allochthonous inputs of DOM and nutrients. We applied absorbance and fluorescence spectroscopy to analyze the chromophoric and fluorescent dissolved organic matter fractions (CDOM and FDOM, respectively) in order to characterize DOM quality across a spatial–temporal scale.

Our investigation started a few weeks before the eruption of the Puyehue–Cordón Caulle and therefore our survey allowed us to record and discuss the effects of this stochastic event. The study area received pumice and ash that deposited on the vegetation and soils, being rapidly transported to the streams and lakes after heavy rainfall events.

Our main hypothesis is that DOM and nutrients in the streams are enhanced substantially by runoff during precipitation events. The terrestrial DOM input is received by pulses into the streams and is determined by the frequency and intensity of precipitation. In this context, the main input expected will be delivered during the austral autumn–winter period when the maximum rainfall is recorded in northwestern Patagonia (Paruelo et al., 1998b). We hypothesize also that given the homogeneity of the streams' subcatchments, which have similar vegetation cover and structure, the four systems will have similar DOM dynamics, in terms of concentration and quality. Regarding the impact of the volcanic eruption in the streams, we do not expect dramatic changes as observed in streams close to the PCC. However, we hypothesize that some parameters such as total suspended solids, nutrient concentration, and the amount and quality of DOM may reflect the deposition and transport of volcanic material.

2. Material and methods

2.1. Study sites

This study was conducted in four mountain streams, Casa de Piedra, De la Virgen, Goye and López (Fig. 1), located in the Glacial Lake district of the Southern Andes (Iriondo, 1989), inside the Nahuel Huapi National Park (Patagonia, Argentina). The streams belong to the catchment of the Lake Moreno complex, a double basin ultraoligotrophic system (41° 04′S, 71° 31′W) that flows into Lake Nahuel Huapi. López stream flows into Lake Moreno West while Casa de Piedra, De la Virgen and Goye flow into Lake Moreno East (Fig. 1). The four streams drain mountain areas covered by a deciduous forest of *Nothofagus pumilio* and piedmont areas with the evergreen trees *Nothofagus dombeyi* and *Austrocedrus chilensis* (Bessera and Moretti, 1993). The vegetation in the area is typical from the xeric border of the temperate rain forest present at both sides of the Andes near 40°S (Daniels and Veblen, 2003; Albariño et al., 2009). The dominant soils of the catchment correspond to the order Andisols with deposits of volcanic ash and pyroclastic products and high water retention capacity (>35%) (Bessera and Moretti, 1993). The streambeds are characterized by a dominance of cobble–boulder substrates. Previous studies including streams of the area have reported low concentrations of nutrients, low conductivity, neutral pH and high levels of dissolved oxygen (Bessera and Moretti, 1993; Pedrozo et al., 1993; Garcia and Añón Suárez, 2007).

2.2. Water sampling and field measurements

The four streams were sampled monthly from May 2011 until September 2013. In each stream, one sampling station was set up in the proximity of the outflow point. Water flow measurements were performed using a flowmeter (Global Water, USA). Temperature, dissolved oxygen and conductivity were measured in situ with an YSI 85 (USA) multiprobe, and pH was measured with a Hanna HI98150 (USA) probe. The epilithon community was sampled from rocks collected from each sampling site in each of the four streams. Four rocks of similar size and shape were collected in each stream and were stored individually in plastic bags inside a cooler and taken to the laboratory where epilithon was brushed off to perform the chlorophyll *a* (chl *a*) concentration measurements.

Subsurface water samples were obtained using acid-washed polycarbonate carboys (5 L) and rinsed in situ with stream water before water collection. The samples were immediately transported to the laboratory, thermally insulated and in darkness.

Meteorological data of the study period was downloaded periodically from an automated weather monitor (Davis Vantage Pro) located at the EMMA Met-Station (Laboratorio de Fotobiología, INIBIOMA, CONICET-UNComahue; 41°7′43.33″S; 71°25′12.03″W; 800 m a.s.l), close to the sampling site at Casa de Piedra stream. Rainfall was quantified as the total precipitation recorded per day (mm/day).

2.3. Laboratory analysis

2.3.1. Nutrient, chlorophyll a and suspended solid determinations

In the laboratory, a volume of 500 mL of the water sample was separated for the determination of total phosphorus (TP) and total nitrogen (TN). TP was measured using the ascorbate-reduced molybdenum blue technique (APHA, 2005). TN was determined after digestion with alkaline solution of potassium persulfate in 1.5 N sodium hydroxide, and subsequent absorbance measurement of nitrate using a UV–visible spectrophotometer (Hewlett–Packard 8453, USA), following Bachmann and Canfield (1996). Total suspended solid concentration (TSS) was determined by filtering a volume of 3 L of whole stream water onto pre-combusted and pre-weighed glass fiber filters (Munktell MF/F 0.7 μm). Finally, the filters were dried at 80 °C for 48 h and weighted. TSS concentration was calculated as the difference between the final and initial mass of the filters divided by the volume of the filtrate (APHA, 2005).

The epilithon was sampled by removing the biofilm from the rocks' surface using a small nylon brush and rinsing with distilled water to obtain a sample of ~100 mL. After homogenizing the sample by manual shaking, 1 mL aliquot was separated for chl *a* extraction with 90% ethanol (Nusch, 1980). After extraction the sample was scanned between 665 nm and 750 nm in a UV–visible spectrophotometer.

2.3.2. Dissolved organic matter characterization

Water samples of each stream were filtered through 0.7 μm glass-fiber filters (Munktell MF/F) and then sterilized by filtration through 0.22 μm PVDF membranes (Millipore) for DOC determination and optical characterization of DOM. Dissolved organic carbon concentrations were measured with a Shimadzu TOC-L high temperature analyzer suited with a high sensitivity catalyst (detection limit of 4 μg/L), to determine non-purgeable organic carbon (NPOC). The mean DOC concentration

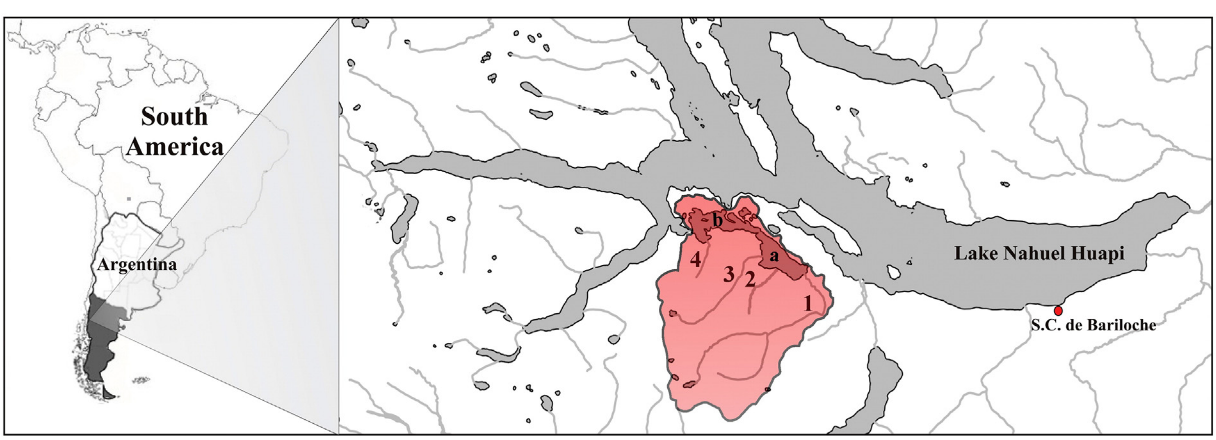


Fig. 1. Geographic location of four studied mountain streams inside the Nahuel Huapi National Park (Patagonia, Argentina). 1) Casa de Piedra; 2) De la Virgen; 3) Goye; 4) López. The area in pink depicts the Lake Moreno complex catchment (a: Lake Moreno East; b: Lake Moreno West) and the four tributary streams. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

resulting from each DOC measurement corresponds to the average of 3–5 injections of 400 μL with a coefficient of variation (CV) lower than 2%.

The absorbance spectra (200 to 800 nm) from filtered (Millipore, PVDF membranes, 0.22 μm) water samples were obtained at 1 nm intervals in a UV–visible spectrophotometer (Hewlett–Packard 8453), using a 100 mm quartz cuvette. ASTM1 grade water (Milli-Q) was used as reference blank, subtracting it from each sample spectrum. The averaged UV–visible absorbance between 700 and 800 nm was subtracted from each spectrum to correct for offsets due to several instrument baseline effects (Helms et al., 2008). All absorbance data was converted to absorption coefficients as follows:

$$a = 2.303\ A/l;$$

where

a Napierian absorption coefficient (m^{-1})
A absorbance
l cuvette's path length (m).

The absorption at 350 nm (a_{350}) was applied to analyze terrestrial CDOM signals. This coefficient is a quantitative measure of CDOM concentration and was chosen based on its suitability to estimate DOC, lignin concentrations and inputs of terrestrial DOM (Hernes and Benner, 2003; Spencer et al., 2008; Walker et al., 2013). For comparative purposes, the a_{350} was normalized by DOC concentration (a_{350}/DOC), after Fichot and Benner (2012).

The spectral slopes for the intervals 275–295 nm ($S_{275–295}$) and 350–400 nm ($S_{350–400}$) were calculated by fitting the log-transformed spectral data to a linear model. The resulting slopes were expressed as positive numbers according to a mathematical convention. The $S_{275–295}$ differs between CDOM sources (Stedmon et al., 2011a; Fichot and Benner, 2012) and has been shown to be inversely correlated to the average molecular weight of DOM (Helms et al., 2008). High molecular weight CDOM presents comparatively lower $S_{275–295}$, indicative of a terrestrial source. In contrast, low molecular weight CDOM has higher $S_{275–295}$ which indicates a more degraded and/or autochthonous source (Helms et al., 2008; Stedmon et al., 2011a; Fichot and Benner, 2012). The slope ratio (S_R) was calculated as the ratio of $S_{275–295}$ to $S_{350–400}$ and was used as a proxy of the relative molecular weight/size and source of the DOM, with lower values indicative of DOM of higher molecular weight (Helms et al., 2008; Spencer et al., 2010; Osburn et al., 2011).

For the analysis of fluorescent DOM (FDOM) the filtered water samples (Millipore, PVDF membranes, 0.22 μm) were scanned in a spectrofluorometer Perkin-Elmer 55B (USA) equipped with a 150-W Xenon arc lamp and a Peltier temperature controller, using a 10 mm quartz fluorescence cell. The raw excitation–emission matrices (EEMs) were collected at specific excitation wavelengths (240–450 nm, 5 nm intervals) and emission wavelengths (300–600 nm, 0.5 nm intervals). As detailed above, ASTM1 grade water was used as blank. The spectrofluorometer was set up with 10 nm excitation and emission slits and a scan speed of 1500 nm/min. The EEMs were processed using the software FL-WinLab® (Perkin-Elmer). Absorbance spectra (200–800 nm) were used to develop a correction matrix of factors for each EEM using the Matlab toolbox FDOMcorr, accounting for inner filter effects, blank subtraction and normalization to the area under the water Raman peak of the blank at 350 nm. The resulting data was expressed in Raman units (Murphy et al., 2010).

Additionally, the humification index (HIX) and the freshness index (β:α or BIX) were calculated as compositional indicators of DOM. The HIX was calculated as the sum of emission intensities between 435 and 480 nm divided by the sum of the emission intensities between 300 and 345 nm at the excitation of 254 nm, corrected according to Ohno (2002). The HIX value ranges from 0 to 1 with low values indicative of autochthonous DOM and higher values reflecting highly humified organic material, mainly of terrestrial origin (Ohno, 2002; Huguet et al., 2009). The BIX is used to assess the relative contribution of DOM processed by microbiota and was measured as the ratio of the emission intensity at 380 nm divided by the maximum emission intensity between 420 and 435 nm, at an excitation of 310 nm (Parlanti et al., 2000; Wilson and Xenopoulos, 2009; Fleck et al., 2014). BIX values higher than 0.8 indicate freshly produced DOM of biological or microbial origin, whereas values < 0.6 are indicative of DOM derived from an allochthonous source (Birdwell and Engel, 2010; Walker et al., 2013).

2.4. PARAFAC modeling

Parallel factor analysis (PARAFAC) was performed using the DOMFluor toolbox for MATLAB software (MATLAB®R2014a, The Natick, USA), according to Stedmon and Bro (2008). A total of 131 EEMs were used to run the PARAFAC, 120 EEMS obtained from samples collected in the four streams and 11 additional EEMs from samples collected across an altitudinal range in Casa de Piedra stream (data not presented here). The Raman and Raleigh scatters were removed from the analysis according to Stedmon and Bro (2008). An exploratory analysis using non-negative constraints was performed to identify outliers. Seven samples identified as outliers were removed from the dataset based on detected instrument errors, artifacts, or striking differences with other samples, determined by calculating a leverage < 0.5 using DOMfluor. Model components were split-half validated (Stedmon et al., 2003; Cory and McKnight, 2005; Stedmon and Bro, 2008). The best model fit was obtained using 10 random initializations. The comparison of the Tucker congruence coefficients (TCC) was done for all the half-splits. The excitation and emission spectra obtained through the PARAFAC modeling were queried against fluorescence spectra included in the open-access database OpenFluor (www.openfluor.org, Murphy et al., 2014), to determine the presence in other studies of the identified PARAFAC components. Components were assumed to be similar, when a minimum similarity score of 0.95 was achieved.

2.5. Data analysis

Data resulting from the different analyses were tested for normal distribution and homoscedasticity. Correlation analysis (Pearson correlation) was applied to study the relationship between chemical parameters in the environmental gradient. Basic descriptive statistics were used (i.e. average and standard deviation) to describe the variability of absorbance and fluorescence values.

A principal component analysis (PCA) was performed including nine variables: precipitation, conductivity, DOC, TP, TN, TSS, and the intensities of the fluorescence components found. The PCA was run with the software CANOCO 4.5 (ter Braak and Smilauer, 1998).

3. Results

3.1. Moreno Lake complex catchment

The catchment of the Moreno Lake complex drains through the Andean streams surveyed in this study: Casa de Piedra, Goye, López and De la Virgen. The larger streams Casa de Piedra (total length: 16.6 km) and Goye (11.4 km) drain catchment areas of ~65.48 km^2 and ~40.22 km^2, respectively. These streams are born in high elevation lakes. Casa de Piedra stream drains the chained lakes Témpanos (1657 m a.s.l) and Jakob (1571 m a.s.l), receiving downslope the Navidad stream which drains Lake Navidad (1800 m a.s.l), while Goye stream is born in Lake Negra (1600 m a.s.l). In contrast, López (3.2 km) and De la Virgen (3.6 km) streams collect water from comparatively smaller catchment areas, 9.46 km^2 and 6.99 km^2, respectively (Fig. 2). They originate directly from the snowpack thaw, receiving also the input of smaller, mostly transient, streams. The headwaters of the Casa de Piedra, Goye and López streams are above the treeline while De la Virgen stream is born below it (>1600 m a.s.l). Overall, approximately 86% of the catchment of Moreno Lake complex drains

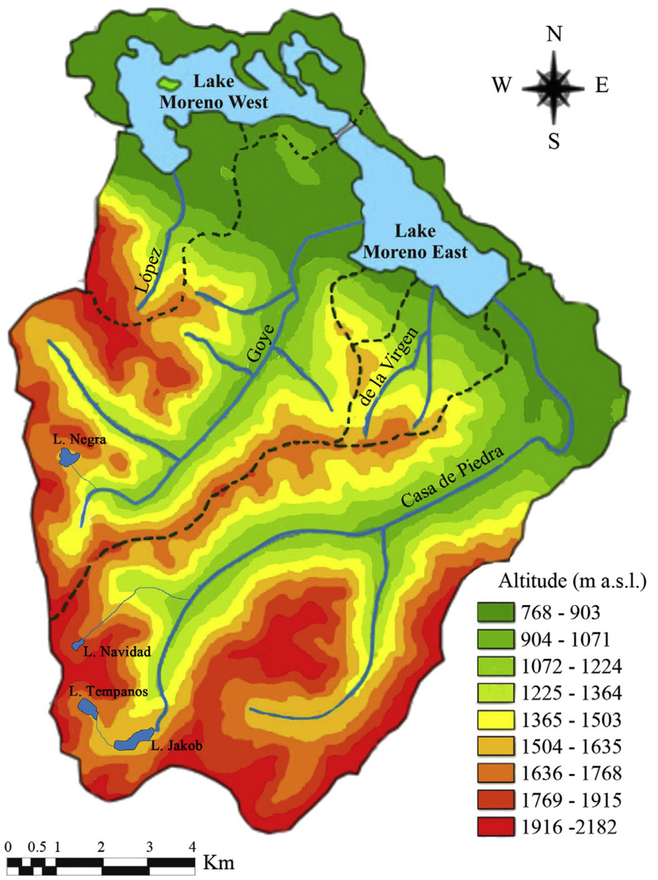


Fig. 2. Lake Moreno complex catchment and the sub-catchments drained by Casa de Piedra, Goye, De la Virgen and López streams (Nahuel Huapi National Park, Patagonia, Argentina).
Map adapted from Queimaliños et al. (2012).

through Casa de Piedra and Goye streams, while the remaining 14% of the area is collected by De la Virgen and López (Fig. 2). The subcatchments have a similar vegetation coverage grading in species composition in the altitudinal range. From 768 m a.s.l (lake level) to 900 m a.s.l, the vegetation is a mixed forest characterized by the occurrence of broadleaf angiosperms such as *Nothofagus dombeyi*, *N. pumilio*, *N. antarctica*, *Lomatia hirsuta* and *Maitenus boaria*, and the gymnosperm *Austrocedrus chilensis*. At increasing elevation, from 900 to 1600 m a.s.l the evergreen forest is replaced by the deciduous *N. pumilio* which dominates the treeline. The

Table 2
Results of the correlation analysis applied to study the relationship between precipitation, water parameters, DOC concentration, a_{350} and components detected by the PARAFAC analysis in four Andean Patagonian streams (Pearson correlation test; * = $p < 0.05$; ** = $p < 0.001$; † = $p > 0.05$; each correlation with n = 21–30).

Variables	Casa de Piedra	Goye	López	De la Virgen
Rain–discharge	0.301†	0.753**	0.852**	0.542**
Rain–TSS	0.353*	0.539**	0.513**	0.562**
Rain–DOC	0.769**	0.774**	0.702**	0.844**
Rain–TP	0.524**	0.255†	0.668**	0.679**
Rain–TN	0.644**	0.356†	0.278†	0.602**
Rain–C1	0.856**	0.789**	0.530**	0.897**
Rain–C2	0.842**	0.737**	0.524**	0.879**
Rain–C3	0.338†	0.420*	0.191†	0.685**
DOC–C1	0.811**	0.896**	0.694**	0.958**
DOC–C2	0.810**	0.898**	0.689**	0.954**
DOC–C3	0.140†	0.266†	0.279†	0.707**
a_{350}–C1	0.944**	0.961**	0.707**	0.977**
a_{350}–C2	0.854**	0.820**	0.595*	0.946**
a_{350}–C3	0.360†	0.414*	0.244†	0.764**
C1–C2	0.945**	0.888**	0.929**	0.987**
C1–C3	0.280†	0.382†	0.143†	0.770**
C2–C3	0.127†	0.227†	0.185†	0.739**

structure of the *N. pumilio* forest changes from the timberline, where single-stemmed erect trees are replaced by multiple-stems irregular growth forms which start to be less continuous upslope where non-forested altoandino vegetation is found.

The survey of the four Andean Patagonian streams showed strong seasonal variation in water temperature; with values between 3 and 5 °C in winter, and summer temperatures around 10–12 °C (Table 1). The conductivity was in general very low throughout the year, fluctuating between 20 and 50 μS in Casa de Piedra, Goye and López streams. In the case of De la Virgen stream, the conductivity was comparatively higher, taking values between 40 and 70 μS (Table 1). Throughout the study, the four streams underwent a decrease in conductivity concomitant with periods of increased precipitation and discharge. The pH values fluctuated in all cases around neutrality, within a range from 6.4 to 7.8 (Table 1). The chl *a* concentration of the epilithon varied between 2 and 12 mg/m^2 throughout the year, with a lowest mean value of 3 mg/m^2 recorded in López stream (Table 1).

Strong positive correlations were found between precipitation and discharge in three out of the four streams surveyed, indicating that precipitation drives the streams' flow (Table 2). The lack of correlation in Casa de Piedra, the stream with the highest discharge, was likely due to the underestimation of the flow during periods of extremely high discharge and current that prevented the regular sampling across the perpendicular stream profile. During the study period, 67% of the

Table 1
Water parameters and chlorophyll *a* (Chl *a*) concentrations due to epilithon recorded in the four mountain streams draining the catchment of the Moreno Lake complex. Values are means (1SD). Units: temperature (°C); conductivity (μS); Chl *a* = chlorophyll *a* concentration due to epilithon (mg/m^2).

Streams		Summer (Dec 21/Mar 20)	Autumn (Mar 21/Jun 20)	Winter (Jun 21/Sep 20)	Spring (Sep 21/Dec 20)
Casa de Piedra	Temperature	10.8 (2.4)	5.2 (1.9)	3.8 (0.7)	6.9 (2.7)
	Conductivity	37.1 (12.9)	41.2 (9.9)	40.9 (11.0)	32.2 (6.7)
	pH	7.5 (0.6)	6.7 (0.8)	7.5 (0.3)	7.6 (0.3)
	Chl *a*	7.9 (2.8)	9.2 (5.6)	8.1 (2.3)	6.9 (1.6)
Goye	Temperature	11.7 (2.8)	5.8 (2.6)	4.4 (1.0)	6.8 (1.4)
	Conductivity	30.2 (8.2)	33.6 (9.9)	36.0 (9.5)	27.7 (14.1)
	pH	7.3 (0.2)	6.7 (0.7)	7.4 (0.6)	7.7 (0.4)
	Chl *a*	6.2 (1.9)	5.1 (3.7)	8.5 (2.4)	6.0 (3.2)
López	Temperature	10.8 (2.6)	5.5 (2.3)	4.0 (1.0)	6.8 (3.0)
	Conductivity	29.6 (10.4)	43.6 (13.0)	46.7 (17.0)	27.1 (12.3)
	pH	7.3 (0.4)	6.8 (0.6)	7.5 (0.6)	7.5 (0.3)
	Chl *a*	3.0 (0.8)	4.3 (2.3)	3.7 (1.5)	2.8 (1.4)
De la Virgen	Temperature	10.2 (1.8)	5.5 (1.6)	4.5 (0.9)	7.5 (3.0)
	Conductivity	64.6 (6.1)	68.1 (10.6)	56.6 (11.5)	45.3 (13.6)
	pH	7.4 (0.2)	6.7 (0.6)	7.4 (0.5)	7.5 (0.2)
	Chl *a*	10.1 (4.8)	9.6 (3.6)	6.0 (2.4)	4.3 (1.0)

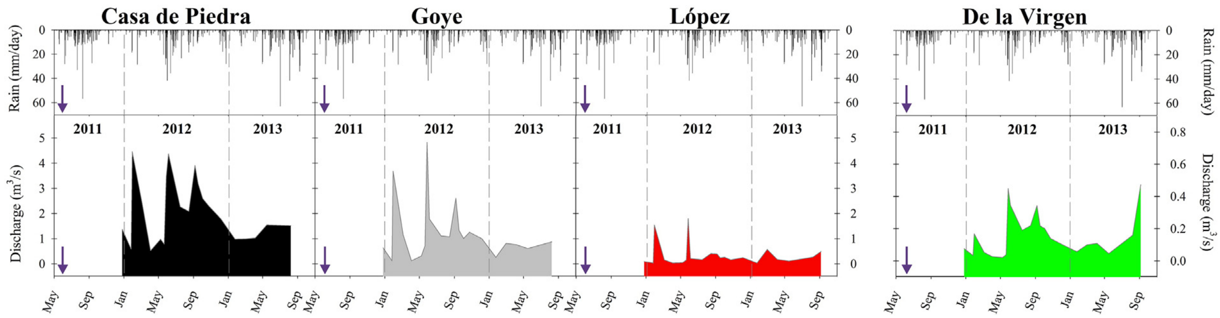


Fig. 3. Daily precipitation volume (upper panel) and discharge (lower panel) in four Andean Patagonian streams during the study period. The arrow indicates the eruption of the Puyehue–Cordón Caulle volcanic complex on 4th June 2011.

total annual precipitation was concentrated within the fall–winter period (April to September), promoting high flows in all the streams (Fig. 3). Casa de Piedra and Goye had the higher flows, with discharge values ranging from 0.1 to 4.8 m^3/s. In contrast, López and De la Virgen had lower discharges, ranging from 0.02 to 1.8 m^3/s. In all the streams, rainfall events were rapidly followed by the increase in the discharge, and also in the concentration of total suspended solids (TSS) reflecting the contribution of terrestrial material by the runoff (Table 2). Baseline values of TSS in the streams were around 1 mg/L, while during periods of increased runoff the concentration peaked up to 40 mg/L (Fig. 4). In addition, DOC, TP and TN concentrations behaved similarly to TSS (Fig. 4). The DOC concentration was always higher in De la Virgen stream ranging from 0.49 to 2.96 mg/L, with a mean value of 1.0 mg/L. In contrast, Casa de Piedra, Goye and López streams showed comparatively lower DOC concentrations ranging from 0.15 to 1 mg/L, with mean values around 0.5 mg/L (Fig. 4). Baseline nutrient concentrations were very low in all the streams, however, during heavy rainfall events, TP and TN concentrations were up to 10 and 25 times higher, respectively (Fig. 4; Table 2). In the case of TP, the baseline concentrations in all the streams were around 5 μg/L, peaking up to ~50 μg/L during rainfall events. TN baseline concentrations were ~200 μg/L, reaching high values ~500 μg/L during periods of increased runoff (Fig. 4; Table 2). The first rain event of every season was the most important in terms of increasing TSS, DOC and nutrient concentrations, whereas subsequent rains generally produced a lower effect, possibly because major DOC and nutrients pools had been flushed in previous events.

Unexpectedly, no major changes were recorded in TSS, DOC, TP and TN values of water samples obtained after the eruption of the PCC. The records showed a similar pattern than the recorded after precipitation events.

3.2. DOM characterization through absorbance and fluorescence analysis

The CDOM absorption coefficient a_{350} was found to correlate directly with DOC concentration in all the studied streams (Fig. 5). During strong precipitation periods and increased runoff, the values of a_{350} were high, coinciding with increased DOC concentrations.

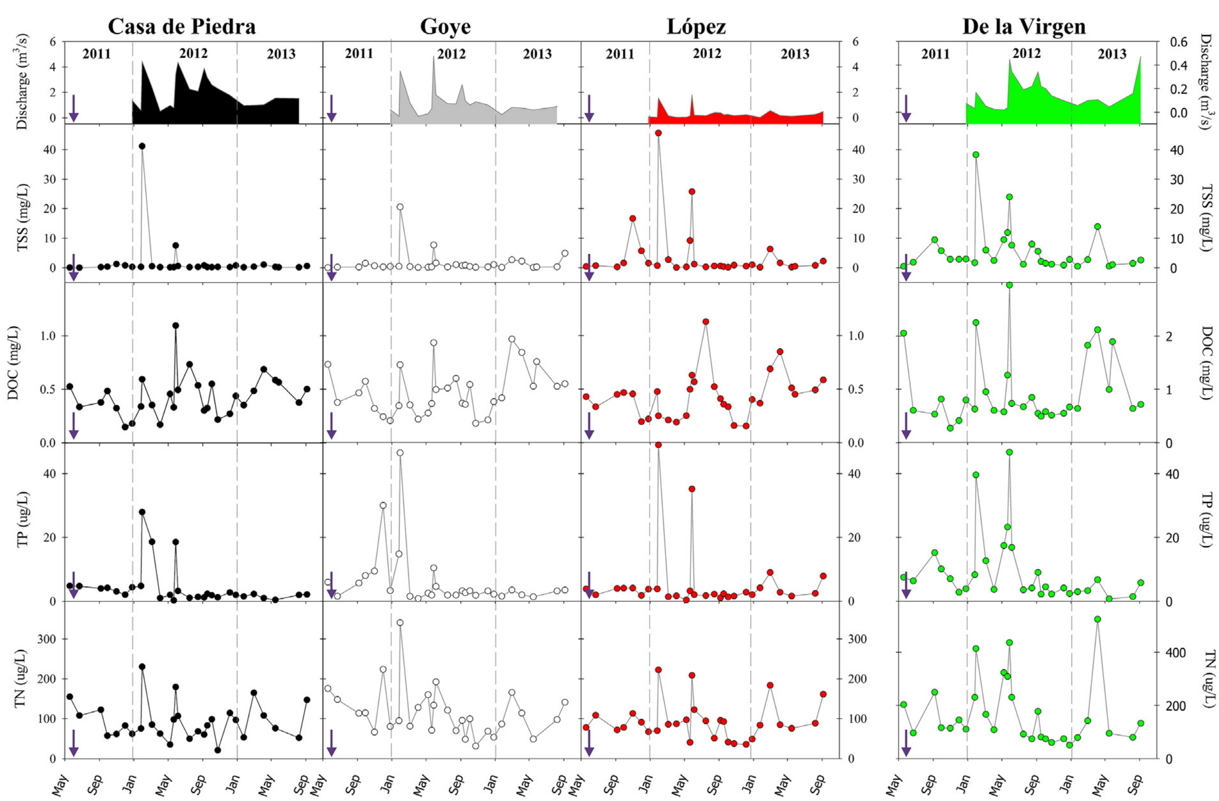


Fig. 4. Seasonal variation in the water discharge (upper panel), and in the concentration of total suspended solids (TSS), dissolved organic carbon (DOC), total phosphorus (TP) and total nitrogen (TN) in four Andean Patagonian streams. The arrow indicates the eruption of the Puyehue–Cordón Caulle volcanic complex on 4th June 2011.

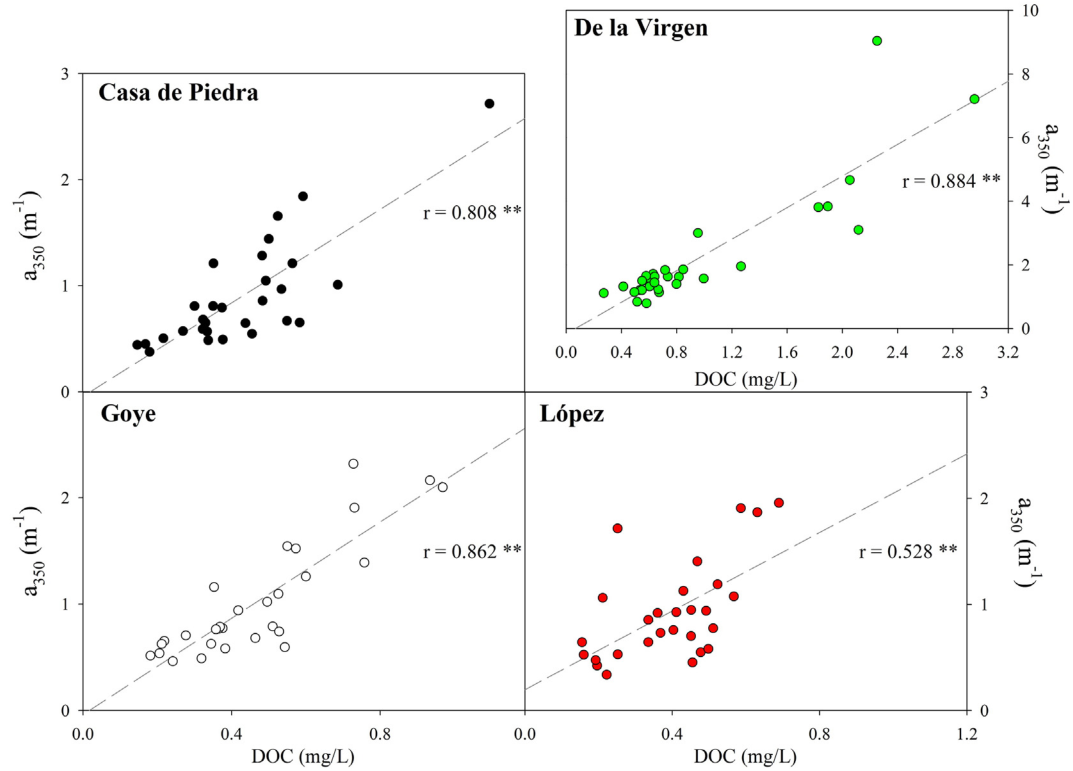


Fig. 5. Relationship between dissolved organic carbon (DOC) concentration and a_{350} in four Andean Patagonian streams ($* = p < 0.05$; $** = p < 0.001$; each correlation with $n = 28–30$).

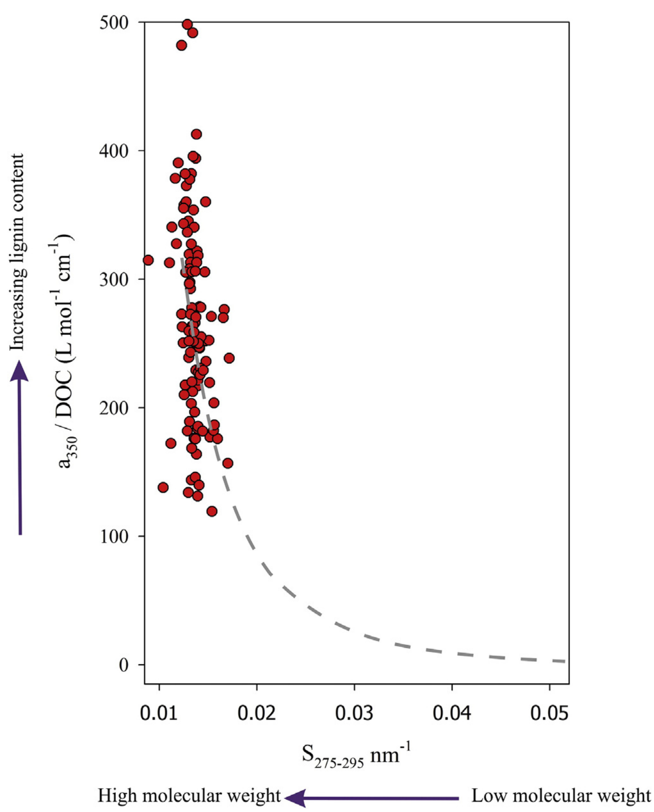


Fig. 6. Relationship between the spectral slope for the intervals 275–295 nm ($S_{275–295}$) and a_{350}/DOC of the four Andean Patagonian streams in a context of the model proposed by Fichot and Benner (2012). The gray dashed line depicts the general model and red dots correspond to the Andean Patagonian streams. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

The relationship between a_{350}/DOC vs. $S_{275–295}$ in the four Andean streams falls at the lower end of the model proposed by Fichot and Benner (2012) for the surface waters of the northern Gulf of Mexico (Fig. 6). In the context of this model, the streams' DOM can be characterized as composed mainly by high molecular weight compounds (low $S_{275–295}$ values) and with variable lignin content (a_{350}/DOC). Likewise, all streams had low S_R values, varying from 0.54 to 1.32, with mean values between 0.76 and 0.99 indicating the presence of high molecular weight and highly aromatic DOM.

The humification index (HIX) of the stream' samples ranged between 0.8 and 1, with mean values ~ 0.9 (Fig. 7). The freshness index (BIX) of Andean streams showed mean values of ~0.6 (Fig. 7). The BIX

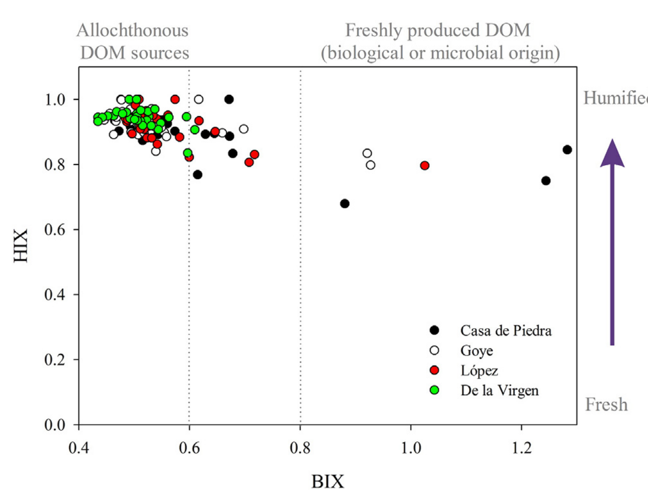
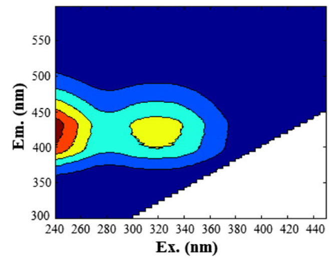
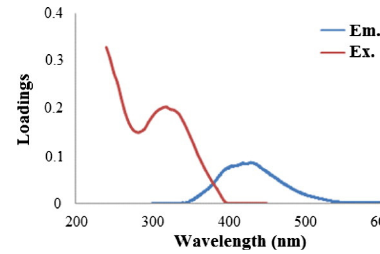
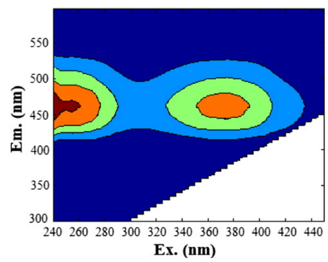
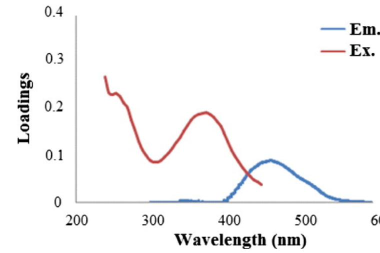
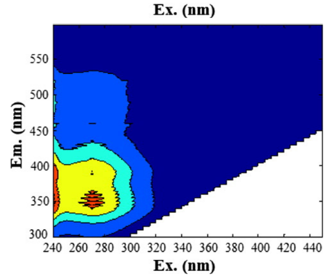
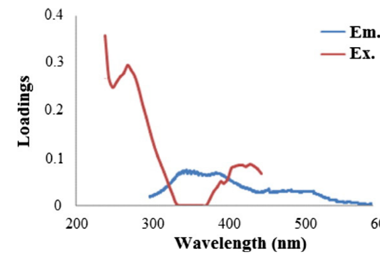


Fig. 7. Relationship between the humification index (HIX) and the freshness index (BIX) in four Andean Patagonian streams. Dotted lines indicate the values reported by Birdwell and Engel (2010) and Walker et al. (2013) and the corresponding DOM characterization.

Table 3
Fluorescence peak locations (secondary peak in parentheses), representative EEMs, and spectral loadings of the three components identified by the PARAFAC model.

Component	Excitation maximum	Emission maximum	EEM	Spectral loadings
1	240 (310) nm	429.5 nm		
2	240 (375) nm	462 nm		
3	270 (410) nm	349.5 (>600) nm		

and HIX showed a strong negative correlation in all the streams (Casa de Piedra $r = -0.623$, $p < 0.001$; Goye $r = -0.5$, $p < 0.05$; López $r = -0.729$, $p < 0.001$; De la Virgen $r = -0.885$, $p < 0.001$), which indicates highly aromatic DOM, supporting other indications about its allochthonous nature. Remarkably, intermediate to high values of the BIX were recorded in all the streams during the spring–summer period of 2011, following the eruption of the PCC.

3.3. PARAFAC

The parallel factor (PARAFAC) analysis of the EEM spectra identified three fluorescent components (C1, C2 and C3) that contribute to FDOM in the four mountain streams (Table 3). The comparison of the components obtained in our survey with components described and archived in the OpenFluor database (Murphy et al., 2014) revealed that C1 and C2 match with humic-like, terrestrially derived material previously identified in a variety of aquatic environments (Stedmon et al., 2011b, 2011c; Osburn and Stedmon, 2011; Yamashita et al., 2011; Cawley et al., 2012; Graeber et al., 2012; Walker et al., 2013, among others). C1 and C2 showed two excitation maxima at a single emission spectrum, as a combination of two fluorescent peaks (Table 3). C1 has a primary excitation peak at 240 nm and a secondary peak at 310 nm with a maximum emission peak at 429.5 nm, and is often referred to as A + M peaks. C2 has a primary excitation maximum at 240 nm and a secondary

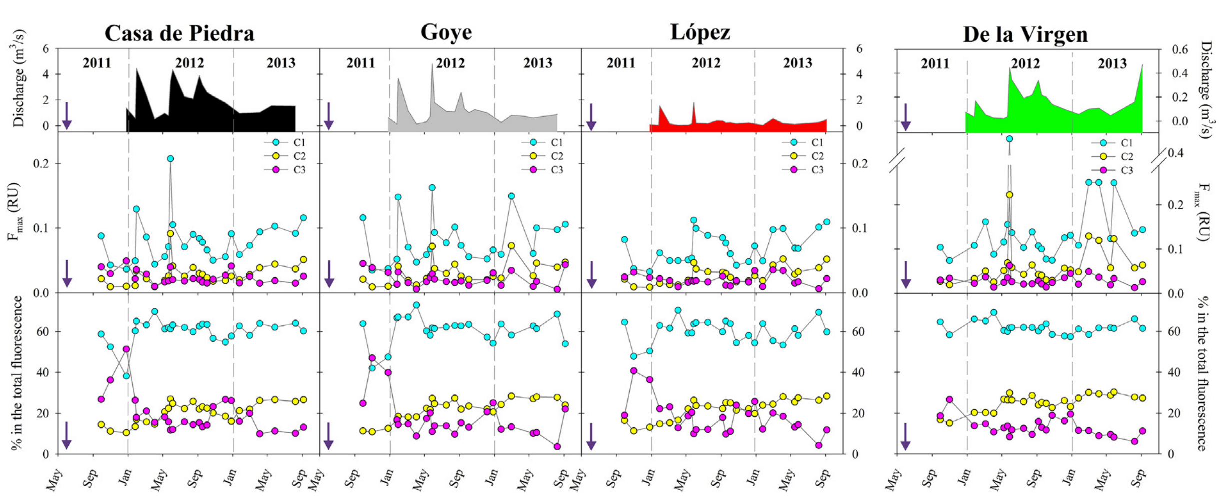


Fig. 8. Streams' discharge (upper panel); fluorescence maximum (F_{max}) of C1, C2 and C3 (middle panel), and the contribution of the three components to the total fluorescence (lower panel) in four Andean Patagonian streams. The arrow indicates the eruption of the Puyehue–Cordón Caulle volcanic complex on 4th June 2011.

peak at 375 nm showing an emission peak at 462 nm, referred to as the A + C peaks (Table 3). All the fluorescent peaks included in the C1 and C2 have been described as humic-like (Coble, 1996, 2007; Stedmon et al., 2003). The C3 spectra did not match accurately with any fluorescent component published in the OpenFluor database. However, the C3 spectra include fluorescent peaks resembling to peaks previously reported for protein-like and pigment-like compounds (Coble, 2007). Like in the cases of C1 and C2, C3 includes apparently a combination of two fluorescent peaks which are in fact not separable by the PARAFAC analysis. The primary excitation peak was found at 270 nm with an emission band at 349.5 nm associated to Tryptophan or T-peak (Coble, 1996; Stedmon et al., 2003; De Laurentiis et al., 2012). The secondary excitation peak was found at ~410 nm with an emission band probably higher than 600 nm, preventing its detection in the emission matrix applied (cutoff at 600 nm) (Table 3). This peak resembles a pigment-like compound as has been described in Coble et al. (1998) and Coble (2007).

The fluorescent intensities of C1 and C2 responded rapidly to changes in the flow after precipitation events (Fig. 8), showing a strong positive correlation with precipitation, DOC concentration and a_{350} in all the streams (Table 2). Higher fluorescent intensities for all components were observed in De La Virgen stream, whereas the three other streams displayed similarly lower intensities (Fig. 8). The FDOM in the four streams surveyed was almost entirely composed by terrestrially derived material as reflected by the intensity of the components C1 and C2. In all the streams, C1 prevailed along the annual cycle, explaining on average ~ 60% of the total FDOM signal. During the spring of 2011, C1 declined to 35–45% perhaps due to the effect of the volcanic deposition. In contrast, the contribution of C3 was almost always low (<10%) except during spring time when it increased up to 20–25%. Component 3 had an exceptional contribution during spring 2011 after the volcanic eruption, reaching ~40–55% in Casa de Piedra, Goye and López and ~30% in De la Virgen. In the latter stream, C3 showed a strong positive correlation with precipitation, DOC, a_{350}, C1 and C2 (Table 2), however, these relationships were not significant in the three remaining streams.

3.4. Multivariate analysis: principal component analysis

The results of the PCA showed that the first two principal components (PC1 and PC2) explained ~75% of the total variance. The first component (PC1) explained ~55%, being positively correlated (>0.6) with C1 (0.92), C2 (0.88), C3 (0.6), DOC (0.87), TN (0.82), precipitation (0.74) and TP (0.72) (Supplementary Fig. S1). The PC2 explained ~20%, being negatively correlated with the conductivity (−0.82). The plot PC1 vs. PC2 shows that precipitation is the main factor explaining the variability of the first axis, whereas the conductivity explained most of the variability of the second axis (Supplementary Fig. S1). Most sampling dates showing precipitation values higher than 5 mm/day are placed on the right side of the plot, and can be characterized by a relative high concentration of DOC, nutrients, C1, C2 and C3. These results showed up that precipitation is a strong driver controlling nutrient as well as the DOM concentrations in these streams. The fact that the three components C1, C2 and C3 present the same correlation pattern and high correlation with the PC1, supports the idea that these three components have the same origin.

4. Discussion

The headwaters of the major catchments of Patagonia are located in the high altitudes of the Andes and constitute complex systems of interconnected mountain lakes and streams draining to large and deep piedmont lakes that feed rivers flowing either to the Pacific or the Atlantic oceans (Iriondo, 1989; Modenutti et al., 1998). The biozones of these catchments are clearly delimited by climate, particularly the temperature and precipitation patterns (Paruelo et al., 1998a). The climate in northwestern Patagonia is cold-temperate with precipitation concentrated in the fall–winter period (April to September), showing the highest values in the Andean stretch (Paruelo et al., 1998b). In this investigation we provide a first integrative approach of the interactions between terrestrial and aquatic systems in four mountain streams draining to a double-basin lake, Lake Moreno complex (Figs. 1 and 2). This catchment is a fluvial network with headwaters originating at high altitudes running on high slopes through rocky soils above the treeline. Downslope the streams cross densely forested areas grading from deciduous to a predominantly evergreen *Nothofagus* cover. Lacustrine systems of this catchment have been the focus of several investigations due to their unique limnological features resulting from the combination of extremely low nutrient and dissolved organic carbon concentrations, challenging solar radiation levels that set the conditions for the development of unique and highly endemic aquatic communities (Morris et al., 1995; Queimaliños et al., 2012; Garcia et al., 2015 and the references therein). Little has been investigated about the low order streams connecting the Lake Moreno complex catchment, although these systems have been indirectly recalled as the main channels of the allochthonous inputs to the piedmont lakes (Queimaliños et al., 2012).

Our survey of Andean Patagonian streams provides evidence of extremely low basal nutrient and DOM concentrations, within the lowest levels recorded globally in oligotrophic running water (Dodds et al., 1998). During our survey, Casa de Piedra, Goye and López streams behaved similarly in terms of hydrologic and physico-chemical parameters, showing low baseline conductivity values, extremely low baseline nutrient and DOC concentrations and also low chlorophyll *a* concentrations. In contrast, De la Virgen stream had always higher values of conductivity, TSS, DOC and nutrient concentrations (Table 1; Fig. 4), reflecting the influence of its particular subcatchment, which is completely covered by *Nothofagus* forest. Nevertheless, in a more general environmental frame the stream parameters recorded are low and characteristic of oligotrophic basins (Dodds et al., 1998). This survey shows that the discharge of the four studied streams reflects the local precipitation regime (Fig. 3), and highlights the essential role of precipitation in the exchange of materials within the catchment (Fig. 4; Supplementary Fig. S1). Particulates, nutrients and DOC exhibit a flushing response with significant variation in their concentrations as a function of stream discharge as has been observed in other systems (van Verseveld et al., 2008). The highest levels of TSS, DOC and nutrient concentrations were observed after the first precipitation event in every season. This is in agreement with the observations of Xu and Saiers (2010) showing that the quantities of DOM mobilized by infiltrating water, decrease with rainfall intensity and frequency. The discharge pattern recorded in our investigation falls within the bimodal discharge described in other mountain streams of northern Patagonia, with higher water levels in fall and winter as consequence of the increased rainfall, and in spring following the snowmelt (Albariño et al., 2009; Díaz Villanueva et al., 2010; Modenutti et al., 2010).

The volcanic eruption that occurred on 4th June 2011 delivered coarse and fine material on the catchment affecting terrestrial and aquatic ecosystems of the NHNP (Modenutti et al., 2013; Chaneton et al., 2014; Daga et al., 2014). The impact of the ash deposited was particularly dramatic in the western limit of the park, neighboring the active volcanic complex. Areas located at slightly higher latitudes (South of Lake Nahuel Huapi) received only small amounts of ash (Chaneton et al., 2014), as was the case of the Moreno lake catchment. The ash covered the recently deposited leaf litter coming from the deciduous and evergreen *Nothofagus* forest thus producing the isolation of the soils. Our sampling schedule comprised pre and post eruption dates; samplings were conducted 15 days previous and posterior to the event, the latter influenced by the torrential rains after the eruption (Fig. 3). The surveyed streams did not show any striking change in turbidity, conductivity, TSS, pH, nutrient and DOC concentrations, likely because the high slopes and high current of these low order systems rapidly channelized the volcanic material into the lakes. Thus, our results show that the effects of the volcanic material in the streams were similar and/or undistinguishable from those of precipitation, at least in our sampling dates. In contrast, in piedmont lakes of the NHNP, where the volcanic materials cumulated and had a longer retention time, the ash produced an increase in total suspended solids, light extinction, phosphorus concentration and phytoplankton biomass (Modenutti et al., 2013; Balseiro et al., 2014). A study conducted in streams located in close proximity to the PCC, recorded high inputs of coarse and fine material that produced the damming of the water and an increase in turbidity (Lallement et al., 2014). Several studies have shown that the amount and size of the volcanic ash decreased with the distance to the PCC, explaining the difference in the amount and quality of deposited volcanic material along a southeast gradient (Bermúdez and Delpino, 2011; Chaneton et al., 2014). The impact of the PCC eruption in the Moreno lake complex catchment was low compared with systems located in the western limit of the Nahuel Huapi National Park. Further, the magnitude of the impact of the Puyehue–Cordón Caulle may not be comparable for example with Mount St. Helens'. The eruption of Mount St. Helens produced not only the deposition of pyroclastic material but also the sudden failure of the north face of the volcano, causing a massive avalanche of debris into the Spirit lake and the surge of hypolimnetic water. The concentration of dissolved organic constituents increased in Lake Spirit from dissolution of pyroclastic material, mud and ash (McKnight et al., 1988).

The dynamics of the allochthonous inputs of DOM could be traced accurately through the CDOM and FDOM analyses that provided complementary information about the quality and source of the DOM inputs. The absorption coefficient a_{350}, associated to lignin concentration, was found to increase significantly with DOC in all the streams (Fig. 5), indicating the terrestrial origin of the DOM. Similarly, the low values of S_R coinciding with precipitation events, indicated the input of terrestrial DOM of high molecular weight and aromaticity (Helms et al., 2008; Spencer et al., 2010; Osburn et al., 2011). The mean S_R values obtained in this investigation are similar to values reported from Arctic rivers at the peak of the freshet or blackwater tropical rivers during the onset of the wet season, when they receive substantial allochthonous inputs (Spencer et al., 2009, 2010; Stedmon et al., 2011a). The values of the relationship between a_{350} and DOC found in our survey are at the lower end in a more general environmental context as depicted in the study by Spencer et al. (2009, 2012), due to the extremely low DOC concentration of Andean streams (<2 mg/L; mean range: 0.15–1 mg/L). Despite their extremely low DOC levels, the inputs of allochthonous DOM during precipitation events could be traced through the changes in a_{350} values.

The non-linear relationship between $S_{275-295}$ vs. a_{350}/DOC proposed by Fichot and Benner (2012) and used as a dual tracer of terrestrial DOM (high lignin content and high molecular weight) and photobleaching processing can be useful to situate the Andean streams in a wider environmental context. In this model, the Andean streams fall in the range of high molecular weight DOM with variable lignin content. This pattern reflects the influence of the inputs from the catchment, not yet transformed by photochemical processing. In fact, in first order streams traversing steep landscapes of the region, as is the case of the studied systems, the leaf litter is rapidly transported downstream thereby having a short residence time to allow leachate, and physico-chemical and biological degradation inside the streams (Albariño et al., 2009), all processes known to affect DOM concentration and character (Jaffé et al., 2008).

Although there is not a universal relationship between DOM concentration and quality (Inamdar et al., 2012), in systems with a unique or dominant DOM source, as the Andean Patagonian streams, a direct relationship between DOM concentration and FDOM can be established (Del Vecchio and Blough, 2004; Catalan et al., 2014). Two humic-like (C1 and C2) and one protein-like (C3) components were found to be present along the year in the four streams. C1 was the dominant fluorescent component (i.e., the component exhibiting the highest fluorescent intensity), followed by C2. The intensities of both humic-like components have a strong positive correlation between each other and with precipitation, DOC, and a_{350} related to dissolved lignin content (Fig. 8, Table 2). Fluorescence in the regions of C1 and C2 is often referred to as the M and C humic-like peaks respectively (Coble, 2007). C1 has been recalled as fulvic-like compounds of low molecular weight and related to microbial processing (Hur et al., 2009), thereby suggesting that the allochthonous DOM received from the catchment has been previously processed in the soils. This component has been commonly attributed to low molecular weight compounds from terrestrial plant or soil organic matter, associated with biological activity (Hur et al., 2009; Fellman et al., 2010; Ishii and Boyer, 2012). The C2 has been recalled as a humic-like component of terrestrial origin (Ishii and Boyer, 2012) with an aromatic chemical nature and of higher molecular weight compared to C1 (Coble, 2007; Fellman et al., 2010, among others). Also, the high HIX values (>0.8; Fig. 7) recorded year round in all the streams are indicative of highly humified DOM (Ohno, 2002; Huguet et al., 2009).

The C3 appears as a combination of protein-like and pigment-like fluorophores not separable by the PARAFAC (Table 3). The protein nature of C3 is clearly deducted from the Ex/Em pattern attributable to tryptophan or T-peak. This Ex/Em has been also attributed to other non-proteinaceous molecules like phenolic moieties, important precursors of humic substances (Maie et al., 2007). The presence of another fluorophore in C3 could be inferred by the second excitation peak found at 410 nm. Such excitation peak is related perhaps with an emission peak beyond 600 nm as has been reported for pigment-like fluorophores (Coble et al., 1998; Coble, 2007). However, the EEM emission range (up to 600 nm) did not allow the detection of the secondary emission peak. C3 was in lower proportion than C1 and C2 within the year, however underwent a springtime increase in intensity in all the streams. The presence of C3 may reflect the leachate of litterfall activated in the soils during spring and conducted to the streams by the progressing snowmelt, as been observed also by Ågren et al. (2008). The recent contribution of litterfall leachates is inferred by the increase in the protein/phenolic fluorophores (Maie et al., 2007; Hur et al., 2009), associated with compounds from the degradation of chlorophyll, possibly phaeopigments known as pigment-like fluorophores (Coble et al., 1998; Coble, 2007). In between rainfall events, temperature influences the production and decay of potential mobile organic matter by controlling microbial activity, in turn affecting the production and leaching of DOC (Andersson et al., 2000; Xu and Saiers, 2010). Therefore, changes in MOD quality during spring time may be due to the increase in terrestrial microbial activity through soil warming that reactivates the decomposition processes, thereby enhancing the production of degradation plant materials which fluoresce likewise proteinaceous or phenolic materials (Maie et al., 2007). Then, the observed changes in DOM quality during spring likely represent a different breakdown stage and/or microbial processing upon the allochthonous DOM, as was observed by Hur et al. (2009). In that investigation, leaf litter incubations with microbiota showed a decrease in a protein-like peak (comparable to our C3), while the fulvic (comparable to our C1) and humic (our C2) peaks were both enhanced after the incubation. The high intensity values of C3 after the volcanic eruption (spring 2011) match with the high BIX values due to the presence of larger amounts of litterfall in the soils, probably due to the defoliation of the surrounding forest (Chaneton et al., 2014) and the increase of dissolved organic compounds obtained through the leaf litter leachate. Besides, changes in the composition of soil microbiota influencing the microbial processing of organic materials in the soils could be expected after the volcanic eruption, having in account that the material deposited induced a disruption in aquatic microbial assemblages (Elser et al., 2015). This disruption may have influenced as well the microbial transformation of proteinaceous and/or phenolic materials (C3) into fulvic and humic acids in the soils, as was observed in spring–summer 2011 by the exceptional contribution of C3 in the streams.

Our investigation reveals that the four first order ultraoligotrophic streams mobilize allochthonous DOM from the catchment into the double basin Lake Moreno. Litterfall of the endemic *Nothofagus* species, deciduous (*N. pumilio*) and evergreen (*N. dombeyi*), is likely the main source of organic matter to the soils of the catchment. During fall, precipitation collects materials from the catchment delivering pulses of particulates, nutrients and DOM composed mostly of humic compounds into the streams. During spring, snowmelt collects a mixture of humic, proteinaceous/phenolic and pigment-like compounds from the leaf litter leachates and products of the increasing microbial activity.

The studied streams act mostly as channels for the materials from the catchment. Their high slope, high current and prevailing low temperatures may favor the rapid export of the materials downstream which are likely transferred to lake food webs rather than to the internal production. The essential role of precipitation in the exchange of materials within the catchment reveals the vulnerability of these aquatic systems to fluctuations in the climate. North Patagonia is experiencing changes in precipitation and temperature, particularly the pronounced fluctuation in the frequency and intensity of rainfall is affecting the hydrological cycles (IPCC, 2007a,b; Marengo et al., 2009), while the rise in temperature is causing the glacial melt (Masiokas et al., 2008). Precipitation and temperature patterns are factors affecting the DOM pool in soils and aquatic systems thereby regulating their dynamics (Häder et al., 2007; Larsen et al., 2011; Sadro and Melack, 2012; Williamson et al., 2014). Moreover, the high levels of UVR impacting on the region also create conditions affecting at different scales in both terrestrial and aquatic systems (Diaz et al., 2006; Häder et al., 2007, 2011; Marinone et al., 2006).

Pronounced drought experienced during the last decade (Villalba et al., 2012) may compromise the amount and quality of the materials exported from the catchment. Besides, forest fires, mass movements, and volcanic events, among other impacts in the landscape would logically reflect on the streams and lakes downslope.

Our results provide the first evidence of the allochthonous DOM inputs through the four main tributaries to the Lake Moreno complex, with complementary and converging evidence resulting from the CDOM and FDOM analyses. Thus, even in extremely clear systems as the mountain streams surveyed, absorbance and fluorescence spectroscopic proxies provide a fair characterization of the DOM pool, allowing detecting the source and processes influencing its seasonal fluctuation.

Overall, our investigation presents clear evidence on the role of the precipitation regime as a driver of the hydrology, the magnitude and the quality of the allochthonous inputs into the tributaries draining the catchment. The described pattern may also apply to other headwaters of Andean Patagonia as it is apparently common to large and deep lakes, shallow lakes and first order streams of the region. This investigation underscores the linkage between terrestrial and aquatic ecosystems in remote, pristine regions of the world in which climate change is the main factor influencing the dynamics of natural ultraoligotrophic aquatic environments.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.03.102.

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