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Assessment of variations in dissolved organic matter in contrasting streams in the Pampas and Patagonian regions (Argentina)

R. D. García[A], *M. L. Messetta*[B], *C. Feijoó*[B] *and P. E. García*[A,C]

[A]Grupo de Ecología de Sistemas Acuáticos a escala de Paisaje, Instituto de Investigaciones en Biodiversidad y Medioambiente, Universidad Nacional del Comahue, CONICET, Quintral 1250, CP8400 San Carlos de Bariloche, Río Negro, Argentina.
[B]Programa de biogeoquímica de ecosistemas dulceacuícolas, Instituto de Ecología y Desarrollo Sustentables, Departamento de Ciencias Básicas, Universidad Nacional de Luján, Route 5 B6702, CP6700 Luján, Argentina.
[C]Corresponding author. Email: garcia.patriciaelizabeth@gmail.com

Abstract. Dissolved organic matter (DOM) is the major source of carbon in aquatic environments and may be derived from allochthonous or autochthonous sources. This study presents the first DOM characterisation in streams from two contrasting Argentinean regions (the Pampas and Patagonia). We found that dissolved organic carbon (DOC) concentrations and absorption coefficients at 254 and 350 nm (a_{254} and a_{350}) were higher in Pampean than in Patagonian streams. DOM from streams in both regions contained compounds with high molecular weight and highly variable a_{350} per DOC; it has been suggested that this could be an indicator of lignin content. The characterisation of DOM reflects the agricultural signal and the effect of autochthonous sources in Pampean streams, whereas a more pristine condition with high input from terrestrial environments was recorded in Patagonian streams. No sign of DOM photodegradation was observed in either region. Fluorescence-based indices suggest a more recent input of DOM in Pampean streams, whereas a highly humified component was recorded in Patagonian streams. The combined use of absorbance and fluorescence-based techniques was useful for understanding the quantity and quality of DOM in these contrasting regions in Argentina.

Additional keywords: allochthonous dissolved organic matter, autochthonous dissolved organic matter, dissolved organic carbon concentration, multivariate analysis.

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Introduction

Fluvial networks link multiple components of the biosphere and transport, process and transform a large quantity of organic carbon (C; Battin *et al.* 2009; Aufdenkampe *et al.* 2011). Most C is associated with dissolved organic matter (DOM) pool, defined as the size fraction below 0.7 µm, primarily derived from terrestrial sources and entering streams through multiple flow pathways from the surrounding landscape (Aitkenhead-Peterson *et al.* 2003; Jaffé *et al.* 2008; Graeber *et al.* 2012). Climatic and hydrogeomorphic variables are usually strong predictors of DOM characteristics in streams, because these features often control terrestrial organic matter storage and hydrological connectivity between catchments and streams (Stanley *et al.* 2012).

Terrestrial DOM input plays an important role in the carbon budgets of catchments, affecting the biogeochemistry and ecology of surface waters (Cole *et al.* 2007; Nilsson *et al.* 2008). The role of hydrology in delivering DOM to streams is affected by land cover (Laudon *et al.* 2011; Larson *et al.* 2014), watershed soils (Hosen *et al.* 2014; Huang *et al.* 2015), the location of the stream in the catchment and landscape topography (Ågren *et al.* 2007). DOM is composed of different organic substances with different reactivity and ecological functions (Benner 2003; Jaffé *et al.* 2008; Aiken 2014). Low molecular weight (LMW) DOM (amino acids, polyamines and nucleotides, among others) has been shown to be directly available for plant and algal uptake (Jones *et al.* 2005; Fransson and Jones 2007; Jansson *et al.* 2012). Similarly, high molecular weight (HMW) DOM is available for microbial assimilation in terrestrial and aquatic environments (Antia *et al.* 1991; Seitzinger and Sanders 1997) and could be susceptible to photodegradation, releasing bioavailable inorganic or LMW organic C, nitrogen and phosphorus for subsequent microbial utilisation (Mostofa *et al.* 2007; Chen and Jaffé 2014).

Recent studies have made extensive use of optical measurements of the chromophoric fraction of DOM (CDOM) to provide useful insights into DOM composition (Fellman *et al.* 2010; Pérez *et al.* 2010; Spencer *et al.* 2012; Gerea *et al.* 2017). CDOM absorbs light in the visible (UV-Vis), ultraviolet (UV)-A and UV-B wavelength ranges, therefore parameters derived from CDOM absorption are powerful tools for distinguishing the composition characteristics of DOM, providing further insights into its source and degradation state across a range of environments (Helms *et al.* 2008; Peter *et al.* 2012; Yates *et al.* 2016).

The Pampas and Patagonia are two contrasting regions in Argentina. Pampean streams are highly productive, with elevated nutrients levels, low current flows and high irradiance because of the lack of riparian vegetation (Feijoó and Lombardo 2007; García *et al.* 2017). Messetta *et al.* (2018) found high levels of dissolved organic carbon (DOC; >5 mg L^{-1}), high DOM humification and aromaticity, suggesting relevant contribution from soils and terrestrial plants to the DOM pool in a Pampean stream. However, these features may also originate from macrophyte breakdown. In contrast, Andean Patagonian catchments are generally characterised by a low nutrient content because of their ultra-oligotrophic condition (Diaz *et al.* 2007; Díaz Villanueva *et al.* 2016), steep slopes favouring high flow in the headstreams (Garcia *et al.* 2015*a*) and typically forested catchments. DOM in Patagonian streams also derives from an allochthonous input, which is highly correlated with precipitation, as suggested by results of fluorescence analysis and high aromaticity (Garcia *et al.* 2015*a*). However, low DOC concentrations (<1 mg L^{-1}) have been found in some streams in the area (Garcia *et al.* 2015*a*). Although both regions are vast and contain different kinds of streams and rivers, there is little information available on DOM quality in either region (Garcia *et al.* 2015*a*).

The aim of the present study was to assess DOM quantity and quality by evaluating variations in the CDOM and fluorescent DOM (FDOM) fractions from streams in two contrasting regions in Argentina (Pampa and Patagonia). Our hypothesis was that differences in DOM concentration and composition between regions are driven by: (1) dominant vegetation in the catchments (grassland for Pampean streams *v.* forested for Patagonian streams); and (2) in-stream autochthonous production. Thus, we expected more indicators of allochthonous sources and a lower DOM processing rate in Patagonian streams because of the low nutrient levels, low temperatures and the presence of riparian forest. In contrast, we expected indicators of an autochthonous source and LMW DOM because of high processing in Pampean streams, associated with algal and macrophyte production.

Materials and methods

Study sites

Pampean region

The Pampa is a vast grassland system covering an area of 500 000 km^2 in central Argentina (Fig. 1*a*). The climate is temperate humid, with a mean annual temperature between 14 and 20°C. Mean annual precipitation ranges from 600 to 1200 mm and is evenly distributed throughout the year, with maximum rainfall in spring and autumn (Vilches and Giorgi 2010). The natural vegetation is grassland, and natural perennial plants are absent except for two species of trees (*Celtis tala* Gill. ex Planch and *Salix humboldtiana* Willd.) that only grow in isolated areas with particular soil conditions. Occasional small forested areas are composed of introduced species (Feijoó and Lombardo 2007).

Pampean streams have low water velocity and their discharge is laminar due to the gentle slope in the region. Streambeds consist of silt and clay without stones or pebbles. High nutrient levels promote the development of rich, dense macrophyte communities that provide substrate for biofilm, as well as food and refuge for macroinvertebrates and fishes (Giorgi *et al.* 2005; Rodrigues Capítulo *et al.* 2010; Ferreiro *et al.* 2014). Owing to the absence of riparian forest, solar radiation reaches the stream bottom, favouring the development of abundant macrophyte and biofilm communities. Furthermore, a potential higher photodegradation process can be expected.

Patagonian region

The sampling area was located in the Glacial Lake district of the Southern Andes (Iriondo 1989), in Nahuel Huapi National Park (Patagonia, Argentina; Fig. 1*b*). The vegetation is similar to temperate rain forest, with deciduous forest of *Nothofagus pumilio* (austral beech) and the evergreen trees *Nothofagus dombeyi* and *Austrocedrus chilensis* in piedmont areas (Daniels and Veblen 2003). The area is characterised by a transitional oceanic–continental cold climate with a dry summer. Mean annual precipitation is ~1800 mm and the mean annual temperature is ~6°C (Paruelo *et al.* 1998; Rapacioli 2011).

Streambeds are dominated by cobble–boulder substrates. Previous studies of streams in the area reported low concentrations of nutrients and C, low conductivity, neutral pH and high levels of dissolved oxygen (García and Añón Suárez 2007; Garcia *et al.* 2015*a*; Díaz Villanueva *et al.* 2016). Most of the study streams belong to the Limay catchment area, which drains into the Atlantic Ocean.

Water sampling and field measurements

This study analysed 38 streams in the Pampas region and 30 in the Patagonian region. The Pampean streams were sampled during February 2016, whereas the Patagonian streams were sampled between December 2016 and February 2017.

At each sampling date, stream discharge (Q) was determined by the velocity–area method (Gordon *et al.* 1992) using a multiprobe anemometer (MiniAir 20; Schiltknecht, Gossau, Switzerland) in Pampean streams and a flowmeter (FP101; Global Water Instrumentation, Sacramento, CA, USA) in Patagonian streams. Conductivity, pH and temperature were measured *in situ* in each stream using a HQ40D multiprobe (Hach Company, Loveland, CO, USA) for Pampean streams and HI98150 (Hanna Instruments, Woonsocket, RI, USA) and YSI85 (Yellow Springs, OH, USA) multiprobes for Patagonian streams. Subsurface water samples in both regions were collected in acid-washed polycarbonate carboys (5 L) that were rinsed tree times with stream water before sample collection. Samples were kept in the dark and immediately transported to the laboratory and processed.

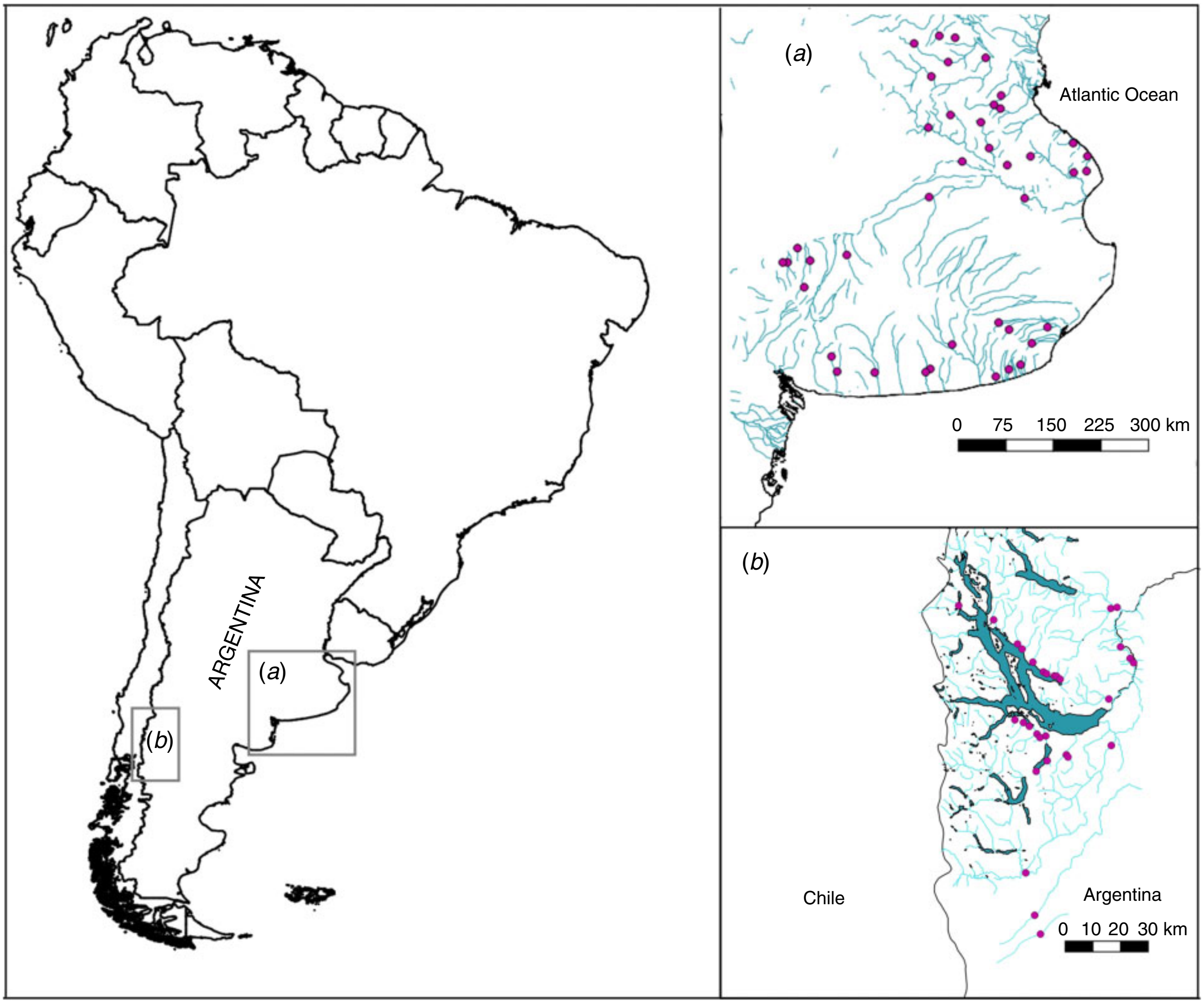

Fig. 1. Map showing the location of the sampling sites (dots) for (*a*) Pampean and (*b*) Patagonian streams.

Characterisation of DOM

Water samples for DOC analysis were collected in amber glass bottles after filtration through precombusted glass fibre filters (0.7 μm; Munktell Filter AB, Falun, Sweden). DOC and dissolved inorganic C (DIC) concentrations were measured in a Shimadzu (Kyoto, Japan) TOC-L analyser for Patagonian samples and in a Shimadzu TOC-V CSH analyser for Pampean samples. All DOC samples were acidified with 10% HCl and preserved at 4°C in the dark until analysis. All samples we measured within 24 h of collection, so the effect of biodegradation was negligible.

DOM was characterised by UV and fluorescence spectroscopy. The absorbance spectra (200–800 nm) from filtered water samples were obtained at 1-nm intervals in a UV-Vis spectrophotometer (Model 8453; Hewlett-Packard, Palo Alto, CA, USA), using a 10-mm quartz cuvette for samples from the Pampas Region and a 100-mm quartz cuvette for samples from the Patagonian region. Milli-Q water was used as the reference blank and subtracted from each sample spectrum. The averaged UV-Vis 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 were converted to absorption coefficients as follows:

$$a = 2.303A \div l$$

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

Absorption coefficients at 254 and 350 nm (a_{254} and a_{350}) were used as an indicator of DOM aromaticity and as an indicator of lignin content (a tracer for terrigenous DOM) respectively (Hernes and Benner 2003; Weishaar *et al.* 2003; Spencer *et al.* 2010; Walker *et al.* 2013). For comparative purposes, the a_{350} was normalised by DOC concentration (a_{350} DOC^{-1}; Fichot and Benner 2012). The absorption ratio at 250 to 365 nm ($E_2 : E_3$) was used to track changes in the relative weight and size of DOM molecules (De Haan and De Boer 1987; Peuravuori and Pihlaja 1997). 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 $S_{275–295}$ is inversely related to DOM molecular size and was used as a proxy for DOM photodegradation (Helms *et al.* 2008; Spencer *et al.* 2010). The slope ratio (S_R) was calculated as the ratio of $S_{275–295}$ to $S_{350–400}$ and was used as a proxy for the relative molecular weight and source of the DOM, with low values indicating higher molecular weight DOM (Helms *et al.* 2008; Guéguen and Cuss 2011).

The FDOM analysis was performed by scanning water samples in a Hitachi F-7000 spectrofluorometer (Tokyo, Japan) for Pampean samples and a Perkin-Elmer 55B spectrofluorometer (Whaltman, MA, USA) for Patagonian samples, using a 10-mm quartz fluorescence cell in both cases. Three fluorescent DOM compositional indicators were used. The humification index (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 an excitation wavelength of 254 nm, following Zsolnay *et al.* (1999), and was used as an indicator of the source, diagenesis and sorptive capacity (Ohno 2002). The freshness index ($\beta:\alpha$ or BIX) was used to assess the relative contribution of DOM processed by microbiota and measured as the ratio of emission intensity at 380 nm divided by the maximum emission intensity between 420 and 435 nm, at an excitation wavelength of 310 nm (Parlanti *et al.* 2000; Wilson and Xenopoulos 2009). BIX values >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). Finally, the fluorescence index (FI) was calculated as the ratio of emissions at 470 nm and 520 nm at an excitation wavelength of 370 nm for corrected spectra, following Cory *et al.* (2010), and used as an indicator of relative autochthonous or microbial versus terrestrial contributions to the DOM pool.

Data analysis

DOM characteristics were compared between regions (Patagonian *v.* Pampean regions) using *t*-tests. All data were previously tested for distribution and homoscedasticity using normality and equal variance tests. Principal component analysis (PCA) was conducted on log-transformed data that were centred and standardised using R framework (ver. 3.3.3, R Core Team, Boston, MA, USA) with FactoMiner package (ver. 1.31.4, Lê, Josse & Husson, Renne, France). Only principal components (PC) with Eigenvalues higher than 1 were considered for the PCA.

Unless indicated otherwise, data are given as the mean ± s.d.

Results

Physicochemical characteristics

As expected, considerable differences were observed in the physicochemical characteristics of the stream water from the two regions. Water temperature was significantly higher in Pampean than Patagonian streams (27.6 ± 3.6 *v.* 7.9 ± 2.5°C respectively; $t = 25.2$, $P < 0.001$). Conductivity exhibited broader variation and was significantly higher in Pampean streams (1971 ± 2461 μS cm^{-1}), with Patagonian streams having extremely low conductivity values (49.3 ± 20.7 μS cm^{-1}; $t = 4.2$, $P < 0.001$). Finally, pH was significantly more alkaline in Pampean than Patagonian streams (8.63 ± 0.50 *v.* 7.40 ± 0.38 respectively; $t = 11.15$, $P < 0.001$). Water flow was higher in Patagonian than Pampean streams (0.94 ± 1.81 *v.* 0.30 ± 0.49 $m^3 s^{-1}$ respectively), although the difference did not reach statistical significance ($t = -1.7$, $P = 0.095$; see Table S1, available as Supplementary Material to this paper).

Table 1. Absorbance and fluorescent-based characterisation of natural dissolved organic matter (DOM) in streams from the Pampas (*n* = 38) and Patagonian (*n* = 30) regions

Data are the mean ± s.d. a_{254}, absorption coefficient at 254 nm; a_{350}, absorption coefficient at 350 nm; BIX, freshness index; CDOM, chromophoric fraction of DOM; DOC, dissolved organic carbon; $E_2:E_3$, ratio of the absorption coefficients at 250 and 365 nm; FDOM, fluorescent DOM; FI, fluorescence index; HIX, humification index; S_R, slope ratio; $SS_{275–295}$, spectral slope for the interval 275–295 nm; $SS_{350–400}$, spectral slope for the interval 350–400 nm

	Pampean streams	Patagonian streams
DOM concentration		
DOC (mg L^{-1})	11.75 ± 4.68	0.62 ± 0.21
CDOM features		
a_{254} (m^{-1})	92.30 ± 63.94	3.31 ± 1.63
a_{350} (m^{-1})	26.62 ± 19.98	0.95 ± 0.51
$SS_{275–295}$ (nm^{-1})	0.014 ± 0.001	0.014 ± 0.002
$SS_{350–400}$ (nm^{-1})	0.013 ± 0.002	0.014 ± 0.003
S_R	1.07 ± 0.14	1.09 ± 0.37
$E_2:E_3$	4.71 ± 0.91	4.52 ± 1.07
FDOM features		
BIX	0.81 ± 0.22	0.61 ± 0.07
FI	1.58 ± 0.06	1.71 ± 0.10
HIX	3.73 ± 2.17	5.58 ± 2.20

DOM characterisation through absorbance and fluorescence

Considerable differences were found in DOM features between regions (Table 1). DOC concentration was significantly higher in Pampean than Patagonian streams ($t = -12.9$, $P < 0.001$). In addition, a_{254} and a_{350} differed significantly between regions, being higher in Pampean than Patagonian streams ($t = -7.6$, $P < 0.001$ for a_{254}; $t = -7.02$, $P < 0.001$ for a_{350}). Conversely, there were no significant differences in spectral slopes $S_{275–295}$ (mean 0.014 nm^{-1} for both regions), $S_{350–400}$, S_R and $E_2:E_3$ between regions ($P > 0.05$; Table 1).

There was a non-linear negative relationship between a_{350} DOC^{-1} and $S_{275–295}$. Values of a_{350} DOC^{-1} were higher and varied more broadly in Pampean than Patagonian streams (18.73–812.64 *v.* 61.36–359.74 L mol^{-1} cm^{-1} respectively). The $S_{275–295}$ was <0.021 nm^{-1} in both regions. Although no significant differences were observed between regions, a broader variation in $S_{275–295}$ was observed in streams in the Pampean region, with the highest a_{350} DOC^{-1} values (Fig. 2).

Both regions had FI values between 1.4 and 1.8 (mean 1.58 ± 0.06 and 1.71 ± 0.17 for Pampean and Patagonian regions respectively; $t = 6.35$, $P < 0.001$), representing a mixture of allochthonous and autochthonous DOM sources. Only a few Patagonian streams showed autochthonous or microbial origin (FI >1.8; Fig. 3*a*). The HIX was higher in Patagonian than Pampean streams (5.58 ± 2.20 *v.* 3.73 ± 2.17 respectively;

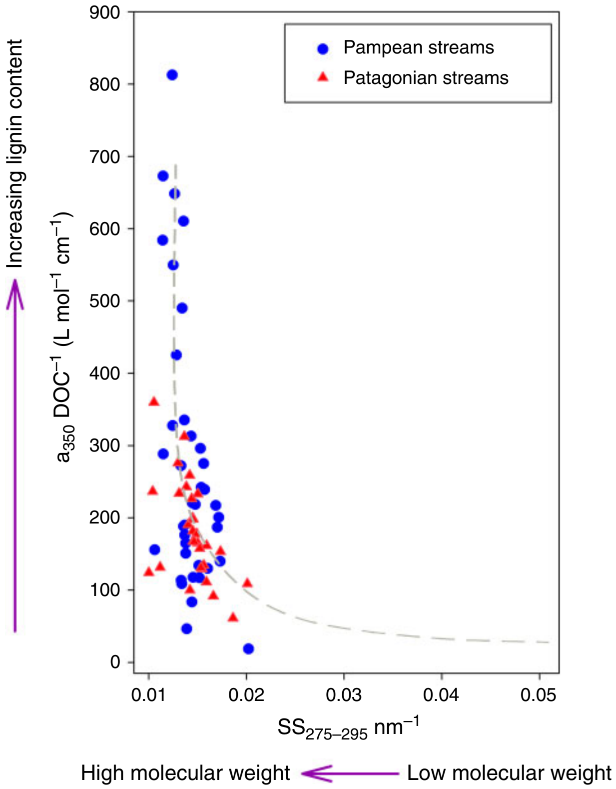

Fig. 2. Relationship between the spectral slope for the intervals 275–295 ($S_{275-295}$) and the absorption coefficient at 350 nm normalised by dissolved organic carbon concentration (a_{350} DOC^{-1}) for streams in Patagonia and the Pampas in the context of the model proposed by Fichot and Benner (2012). The grey dashed line depicts the general model.

$t = 3.45$, $P < 0.001$). Moreover, low (<4) HIX values were observed in most Pampean streams, indicating fresher DOM (Fig. 3*a*). BIX was higher in Pampean than Patagonian streams (0.81 ± 0.22 *v.* 0.61 ± 0.07 respectively; $t = -4.8$, $P < 0.001$); in fact, BIX values were <0.7 for most Patagonian streams (low fresh component), whereas there was greater variation in BIX values in Pampean streams (ranging from 0.6 to 1.8), indicating freshly produced DOM (Fig. 3*b*).

Multivariate analysis of DOM

PCA was used to discriminate different regions with the maximum variation in DOM optical features. The PCA identified three components with Eigenvalues >1 (PC1, PC2 and PC3), which explained 88.14% of the total variance of data (Table S2). PC1 explained 48.78% of the variance and was positively correlated with DOC concentration and the absorption coefficients a_{254} and a_{350}, but was negatively correlated with FI. PC1 clearly separates streams with high DOC concentration and absorption indices (right in both graphs in Fig. 4; Pampean streams) from those with low DOC concentrations (left in both graphs in Fig. 4; Patagonian streams). PC2 explained 20.84% of the variance and was positively correlated with $E_2:E_3$ and $S_{275-295}$. PC2 was characterised by $S_{275-295}$ (lower values indicate an increase in molecular size) and $E_2:E_3$ (indicator of molecular size), both of which are independent of DOC concentration, showing a gradient of molecular size in streams from both regions. Finally, PC3 explained 18.52% of the total variation, with a high positive correlation with HIX and a negative correlation with BIX. PC3 separated streams with more degraded DOM (top in graph in Fig. 4*b*) from those with fresher DOM (bottom in graph in Fig. 4*b*; Table S2).

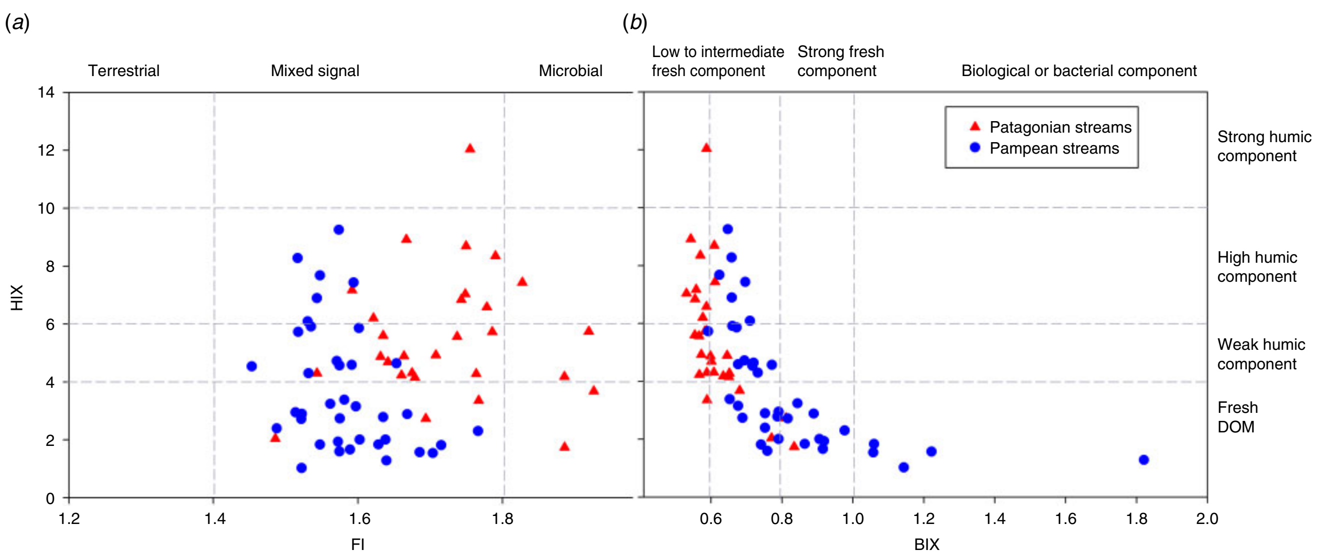

Fig. 3. Relationship between fluorescent dissolved organic matter (DOM) indices: (*a*) humification index (HIX) plotted against the fluorescent index (FI) and (*b*) HIX plotted against the freshness index (BIX). The dashed lines indicate the values reported by Huguet *et al.* (2009) and the corresponding DOM characterisation.

Discussion

This study found high variability in DOM origin and composition, as well as in DOC concentrations, in both Pampean and Patagonian regions (Table 1). DOC concentrations and absorption coefficients (a_{254} and a_{350}) were significantly higher in streams in the Pampas than in Patagonia. It is well known that CDOM is strongly related to DOC concentration (Spencer *et al.* 2007; Helms *et al.* 2008). Higher DOC values in Pampean streams may be related to their higher aquatic productivity (Acuña *et al.* 2011; García *et al.* 2017). Conversely, Andean Patagonian streams are considered to be ultra-oligotrophic environments, with limited nutrients and characterised by low DOC concentrations (Queimaliños *et al.* 2012; Garcia *et al.* 2015*a*, 2015*b*).

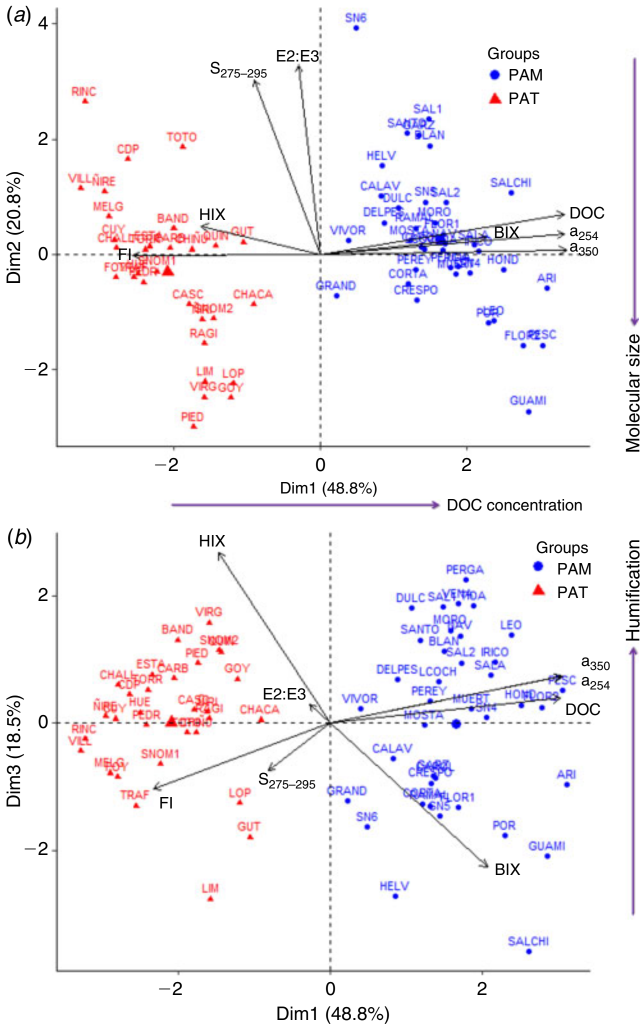

Fig. 4. Biplot showing the results of principal component (PC) analysis depicting the positions of the streams from different regions: (*a*) PC1 *v.* PC2; (*b*) PC1 *v.* PC3. PAM, Pampean streams; PAT, Patagonian streams. Stream abbreviation codes are defined in Table S1. a_{254}, absorption coefficient at 254 nm; a_{350}, absorption coefficient at 350 nm; BIX, freshness index; CDOM, chromophoric fraction of DOM; DOC, dissolved organic carbon; $E_2:E_3$, ratio of the absorption coefficients at 250 and 365 nm ; FDOM, fluorescent DOM; FI, fluorescence index; HIX, humification index; S_R, slope ratio; $SS_{275–295}$, spectral slope for the interval 275–295 nm; $SS_{350–400}$, spectral slope for the interval 350–400 nm.

The DOM in the Pampean streams studied was characterised by high a_{254} and a_{350}, indicative of high aromaticity and HMW compounds. In this context, the broad variation observed in a_{350} DOC^{-1}, also considered a proxy for DOM-related lignin content, suggests an allochthonous source of DOM in Pampean streams. The fluorescence-based DOM indices provide useful supplementary information for studying and comparing the chemical characteristics of DOM between different regions (Fig. 3). FI has been widely used to track autochthonous versus allochthonous DOM in freshwater environments (Hood *et al.* 2005; Miller and McKnight 2010; Williams *et al.* 2010). In this regard, the FI values in Pampean streams could be interpreted as a signal of mixed allochthonous and autochthonous sources. The low HIX values indicate that DOM consists of poorly degraded material. In this region, the humic-like fluorescence may derive from the breakdown of highly productive macrophyte communities (Catalán *et al.* 2013) and biological processes. It is well known that the Pampas region is undergoing a process of agriculture intensification that affects the riparian zone of streams and rivers as a result of the replacement of the original herbaceous vegetation. Agricultural activities increase dissolved nutrient levels in the water, favouring microbiological activity (Feijoó and Lombardo 2007; Amuchástegui *et al.* 2016; Casas-Ruiz *et al.* 2017). Interestingly, the freshness index or BIX showed broad variation in Pampean streams, in which values ranged from 0.6 to 1.8, suggesting that the DOM consists of fresh DOM compounds. As mentioned above, these finding could be explained by the fact that Pampean streams are highly productive and by the presence of aquatic vegetation (submerged and floating macrophytes) and herbaceous litter decomposition, which provide more biodegradable DOM. Our results are in agreement with those of previous studies, which have suggested that CDOM derived from macrophytes usually has lower BIX values (~1), but high absorbance coefficient a_{350} compared with phytoplankton-derived CDOM (Zhang *et al.* 2013).

DOM characterisation of Patagonian streams showed low absorption coefficients a_{254} and a_{350} and low DOC concentrations, which are indicative of the ultra-oligotrophic conditions of these streams (Queimaliños *et al.* 2012; Garcia *et al.* 2015*a*). The high values of a_{350} DOC^{-1} suggest low degradation progresses in both regions. Similar to previous findings in streams from the Patagonian region, the values were distributed more to the left in the model proposed by Fichot and Benner (2012), with high a_{350} DOC^{-1} values and low $S_{275–295}$ values (Garcia *et al.* 2015*a*). In this regard, it is known that DOM in Patagonian streams is derived from an allochthonous source, primarily soil and riparian forest along the catchment (Albariño and Díaz Villanueva 2006; Garcia *et al.* 2015*a*). The FI showed a mixed signal (allochthonous and autochthonous sources); this index provides insight into the source of DOC (McKnight *et al.* 2001). In the present study we found some streams with high microbial signature (Fig. 3); nevertheless, FI values are not as high as those reported for algal leachates or phytoplankton production (FI >2; Korak *et al.* 2015). Conversely, HIX values were high in Patagonian streams, which is indicative of highly humified material, commonly observed in ultra-oligotrophic Patagonian aquatic environments (Garcia *et al.* 2015*a*, 2015*b*; Soto Cárdenas *et al.* 2017). In contrast, BIX values were low (mean value ~0.61), reflecting the small fresh component present in the DOM.

Both regions showed unexpected similarities in relation to DOM characterisation. Values of absorbance-based indicators independent of DOC concentration, such as $S_{275-295}$ (molecular size), $E_2:E_3$ (average molecular size), $S_{350-400}$ and S_R, were similar among streams, suggesting that DOM consists of HMW compounds. This idea is reinforced by the fact that a non-linear relationship was found between a_{350} DOC^{-1} and $S_{275-295}$ (used as a dual trace of terrestrial DOM and photobleaching), indicating that in both regions DOM consists of HMW compounds with highly variable lignin content. In addition, we found that the relationship between a_{350} DOC^{-1} and $S_{275-295}$ for both regions fell at the lower end of the model proposed by Fichot and Benner (2012; Fig. 2). The low variation in $S_{275-295}$ is indicative of the absence of a photodegradation processes. Photodegradation processes are not observed in Pampean streams, probably due to a combination of factors, such as a decrease in water transparency (self-shading or an inner-filter effect), dissolved oxygen concentrations in autumn and summer as a result of livestock in the Pampean region (Amuchástegui *et al.* 2016) or a high humic substances content in some streams (Messetta *et al.* 2018). Conversely, streams in the Patagonian region have high transparency and the water receives high solar radiation levels (Zagarese *et al.* 2001). However, the short residence time of water and low temperature in the region probably do not allow DOM photodegradation processes to take place (Garcia *et al.* 2015*a*).

The PCA was useful for discriminating both region in terms of DOC and absorbance coefficients. Moreover, this analysis can provide signs of interference among the different DOM quality indicators. For example, PC2 sorted the streams according to the molecular size of the DOM ($S_{275-350}$, E2 : E3) and was not related to the degree of humification (HIX) in PC3. This could suggest that DOM size is independent of age in these environments. Previous studies have also suggested interference between CDOM and FDOM indicators, reporting that a peak at 275 nm can affect $S_{275-295}$ in leachates, or that polyphenol-like fluorescence may interfere with HIX and could be interpreted as increasing humification or aromaticity (Cuss and Guéguen 2015). Despite the fact that seasonal variation was not taken into account, the present study emphasises the importance of surrounding landscape in C contribution to lotic environments in both the Pampas and Patagonia regions. In this regard, the effect of hydrology on DOC concentration has been observed previously, suggesting an increase in DOC concentration with increasing discharge (Garcia *et al.* 2015*a*; Messetta *et al.* 2018). Alternatively, LMW aromatic compounds such as polyphenols can be derived from the decomposition of tannin or through the photohumification of LMW compounds from biomass material and increase the CDOM signal (Chen and Jaffé 2014). Throughout the year, the inputs into Patagonian streams are from allochthonous sources, whereas in Pampean streams the source of DOM could shift from a mixture of autochthonous and allochthonous compounds to a more allochthonous humic material during rainfall.

Previous studies have documented significant variations in stream DOM composition under different vegetation types across different climatic regions (Jaffé *et al.* 2008, 2012; Watanabe *et al.* 2012; Yates *et al.* 2016). Some studies have reported that vegetation type and, in some cases, different species have their own optical and fluorescence features (Cuss and Guéguen 2013). Thus, it is generally assumed that lotic DOM is dominated by terrestrial sources (Stanley *et al.* 2012; Stedmon and Cory 2014). The biogeochemical input of DOM is determined by soil and vegetation, but also regulated by hydrology. Indeed, the Patagonian and Pampean regions are very different in this regard. The Pampas region is covered in cropland and grassland (Amuchástegui *et al.* 2016). It is important to note that the Pampean region is undergoing a process of agricultural intensification that could alter the chemical composition and dynamics of DOM; therefore, an increase in the BIX and a decrease in humification can be expected. The Patagonian streams flow through poorly developed soils covered in the endemic *Nothofagus* forest (a type of austral beech) that sheds its leaves in autumn (Garcia *et al.* 2015*a*, 2018).

The results presented in this study are the first records of absorbance and fluorescence-based DOM for Pampean streams, and provide new information on Andean streams in the Patagonian region. The main conclusion of this study is that different landscape features (vegetation, relief, soil composition, irradiation etc.) may explain the differences in DOC concentration, whereas other parameters based on fluorescence data could reflect DOM transformation and source (Fig. 4). As a general result, the comparison of DOM features between regions may be important for the ecosystem function response to changes in terrestrial inputs due to increases in rainfall that could affect stream transparency and thereby DOM dynamics. Sustained environmental monitoring in relation to seasonal variation is required in order to assess the dynamics of the streams in both regions. The data presented herein could provide a useful baseline for characterising DOM in different regions in Argentina, taking into account these values as background levels for future scenarios of climate change.

Conflicts of interest

The authors declare that they have no conflicts of interest.

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References

Acuña, V., Vilches, C., and Giorgi, A. (2011). As productive and slow as a stream can be – the metabolism of a Pampean stream. *Journal of the North American Benthological Society* **30**(1), 71–83. doi:10.1899/09-082.1

Ågren, A., Buffam, I., Jansson, M., and Laudon, H. (2007). Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export. *Journal of Geophysical Research – Biogeosciences* **112**, G03003. doi:10.1029/2006JG000381

Aiken, G. R. (2014). Fluorescence and dissolved organic matter: a chemist's perspective. In 'Aquatic Organic Matter Fluorescence'. (Eds P. Coble, J. Lead, A. Baker, D. Reynolds, and R. Spencer.) pp. 35–74. (Cambridge University Press: New York, NY, USA.)

Aitkenhead-Peterson, J., McDowell, W., Neff, J., Stuart, E., and Robert, L. (2003). Sources, production, and regulation of allochthonous dissolved organic matter inputs to surface waters. In 'Aquatic Ecosystems: Interactivity of Dissolved Organic Matter'. (Eds S. E. G. Findlay and R. L. Sinsabaugh.) pp. 25–70. (Academic Press: San Diego, CA, USA.)

Albariño, R. J., and Díaz Villanueva, V. (2006). Feeding ecology of two plecopterans in low order Andean–Patagonian streams. *International Review of Hydrobiology* **91**(2), 122–135. doi:10.1002/IROH.200510823

Amuchástegui, G., Di Franco, L., and Feijoó, C. (2016). Catchment morphometric characteristics, land use and water chemistry in Pampean streams: a regional approach. *Hydrobiologia* **767**(1), 65–79. doi:10.1007/S10750-015-2478-8

Antia, N. J., Harrison, P. J., and Oliveira, L. (1991). The role of dissolved organic nitrogen in phytoplankton nutrition, cell biology and ecology. *Phycology* **30**, 1–89. doi:10.2216/I0031-8884-30-1-1.1

Aufdenkampe, A. K., Mayorga, E., Raymond, P. A., Melack, J. M., Doney, S. C., Alin, S. R., Aalto, R., and Yoo, K. (2011). Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. *Frontiers in Ecology and the Environment* **9**, 53–60. doi:10.1890/100014

Battin, T. J., Luyssaert, S., Kaplan, L. A., Aufdenkampe, A. K., Richter, A., and Tranvik, L. J. (2009). The boundless carbon cycle. *Nature Geoscience* **2**, 598–600. doi:10.1038/NGEO618

Benner, R. (2003). Molecular indicators of the bioavailability of dissolved organic matter. In 'Aquatic Ecosystems: Interactivity of Dissolved Organic Matter'. (Eds S. E. G. Findlay and R. L. Sinsabaugh.) pp. 121–137. (Academic Press: San Diego, CA, USA.)

Birdwell, J. E., and Engel, A. S. (2010). Characterization of dissolved organic matter in cave and spring waters using UV-Vis absorbance and fluorescence spectroscopy. *Organic Geochemistry* **41**(3), 270–280. doi:10.1016/J.ORGGEOCHEM.2009.11.002

Casas-Ruiz, J. P., Catalan, N., Gomez-Gener, L., Von Schiller, D., Obrador, B., Kothawala, D. N., Lopez, P., Sabater, S., and Marcé, R. (2017). A tale of pipes and reactors: controls on the in-stream dynamics of dissolved organic matter in rivers. *Limnology and Oceanography* **62**(S1), S85–S94. doi:10.1002/LNO.10471

Catalán, N., Obrador, B., Felip, M., and Pretus, J. L. (2013). Higher reactivity of allochthonous vs. autochthonous DOC sources in a shallow lake. *Aquatic Sciences* **75**, 581–593. doi:10.1007/S00027-013-0302-Y

Chen, M., and Jaffé, R. (2014). Photo- and bio-reactivity patterns of dissolved organic matter from biomass and soil leachates and surface waters in a subtropical wetland. *Water Research* **61**, 181–190. doi:10.1016/J.WATRES.2014.03.075

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J., and Melack, J. (2007). Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems* **10**, 172–185. doi:10.1007/S10021-006-9013-8

Cory, R. M., Miller, M. P., McKnight, D. M., Guerard, J. J., and Miller, P. L. (2010). Effect of instrument-specific response on the analysis of fulvic acid fluorescence spectra. *Limnology and Oceanography, Methods* **8**(2), 67–78. doi:10.4319/LOM.2010.8.67

Cuss, C. W., and Guéguen, C. (2013). Distinguishing dissolved organic matter at its origin: size and optical properties of leaf-litter leachates. *Chemosphere* **92**, 1483–1489. doi:10.1016/J.CHEMOSPHERE.2013.03.062

Cuss, C. W., and Guéguen, C. (2015). Characterizing the labile fraction of dissolved organic matter in leaf leachates: methods, indicators, structure, and complexity. In 'Labile Organic Matter – Chemical Compositions, Function, and Significance in Soil and the Environment'. (Eds Z. He and F. Wu.) SSSA Speccial Publication 62, pp. 237–274. (Soil Science Society of America: Madison, WI, USA.). doi:10.2136/SSSASPECPUB62.2014.0043

Daniels, L. D., and Veblen, T. T. (2003). Altitudinal treelines of the southern Andes near 40°S. *Forestry Chronicle* **79**(2), 237–241. doi:10.5558/TFC79237-2

De Haan, H., and De Boer, T. (1987). Applicability of light absorbance and fluorescence as measures of concentration and molecular size of dissolved organic carbon in humic Lake Tjeukemeer. *Water Research* **21**(6), 731–734. doi:10.1016/0043-1354(87)90086-8

Diaz, M., Pedrozo, F., Reynolds, C., and Temporetti, P. (2007). Chemical composition and the nitrogen-regulated trophic state of Patagonian lakes. *Limnologica* **37**(1), 17–27. doi:10.1016/J.LIMNO.2006.08.006

Díaz Villanueva, V. D., Navarro, M. B., and Albariño, R. (2016). Seasonal patterns of organic matter stoichiometry along a mountain catchment. *Hydrobiologia* **771**(1), 227–238. doi:10.1007/S10750-015-2636-Z

Feijoó, C. S., and Lombardo, R. J. (2007). Baseline water quality and macrophyte assemblages in Pampean streams: a regional approach. *Water Research* **41**(7), 1399–1410. doi:10.1016/J.WATRES.2006.08.026

Fellman, J. B., Hood, E., and Spencer, R. G. M. (2010). Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: a review. *Limnology and Oceanography* **55**(6), 2452–2462. doi:10.4319/LO.2010.55.6.2452

Ferreiro, N., Feijoó, C., Giorgi, A., and Rosso, J. (2014). Macroinvertebrates select complex macrophytes independently of their body size and fish predation risk in a Pampean stream. *Hydrobiologia* **740**(1), 191–205. doi:10.1007/S10750-014-1953-Y

Fichot, C. G., and Benner, R. (2012). The spectral slope coefficient of chromophoric dissolved organic matter ($S_{275-295}$) as a tracer of terrigenous dissolved organic carbon in river-influenced ocean margins. *Limnology and Oceanography* **57**(5), 1453–1466. doi:10.4319/LO.2012.57.5.1453

Fransson, A. M., and Jones, D. L. (2007). Phosphatase activity does not limit the microbial use of low molecular weight organic-P substrates in soil. *Soil Biology & Biochemistry* **39**, 1213–1217. doi:10.1016/J.SOILBIO.2006.11.014

García, P. E., and Añón Suárez, D. A. (2007). Community structure and phenology of chironomids (Insecta: Chironomidae) in a Patagonian Andean stream. *Limnologica* **37**(1), 109–117. doi:10.1016/J.LIMNO.2006.09.005

Garcia, R. D., Reissig, M., Queimaliños, C. P., Garcia, P. E., and Diéguez, M. C. (2015*a*). Climate-driven terrestrial inputs in ultra-oligotrophic mountain streams of Andean Patagonia revealed through chromophoric and fluorescent dissolved organic matter. *The Science of the Total Environment* **521–522**, 280–292. doi:10.1016/J.SCITOTENV.2015.03.102

Garcia, P. E., Dieguez, M. C., and Queimaliños, C. (2015*b*). Landscape integration of North Patagonian mountain lakes: a first approach using characterization of dissolved organic matter. *Lakes and Reservoirs: Research and Management* **20**(1), 19–32. doi:10.1111/LRE.12083

García, V. J., Gantes, P., Giménez, L., Hegoburu, C., Ferreiro, N., Sabater, F., and Feijoó, C. (2017). High nutrient retention in chronically nutrient-rich lowland streams. *Freshwater Science* **36**(1), 26–40. doi:10.1086/690598

Garcia, R. D., Diéguez, M. C., Gerea, M., Garcia, P. E., and Reissig, M. (2018). Characterization and reactivity continuum of dissolved organic matter in forested headwater catchments of Andean Patagonia. *Freshwater Biology* **63**(9), 1049–1062. doi:10.1111/FWB.13114

Gerea, M., Pérez, G., Unrein, F., Soto Cárdenas, C., Morris, D., and Queimaliños, C. P. (2017). CDOM and the underwater light climate in two shallow North Patagonian lakes: evaluating the effects on nano and microphytoplankton community structure. *Aquatic Sciences* **79**, 231–248. doi:10.1007/S00027-016-0493-0

Giorgi, A., Feijoó, C., and Tell, G. (2005). Primary producers in a Pampean stream: temporal variation and structuring role. *Biodiversity and Conservation* **14**(7), 1699–1718. doi:10.1007/S10531-004-0694-Z

Gordon, N., McMahon, T., and Finlayson, B. (Eds) (1992). 'Stream Hydrology – An Introduction for Ecologists.' (Wiley: Chichester, UK.)

Graeber, D., Gelbrecht, J., Pusch, M. T., Anlanger, C., and von Schiller, D. (2012). Agriculture has changed the amount and composition of dissolved organic matter in Central European headwater streams. *The Science of the Total Environment* **438**, 435–446. doi:10.1016/J.SCITOTENV.2012.08.087

Guéguen, C., and Cuss, C. W. (2011). Characterization of aquatic dissolved organic matter by asymmetrical flow field-flow fractionation coupled to UV-Visible diode array and excitation emission matrix fluorescence. *Journal of Chromatography. A* **1218**(27), 4188–4198. doi:10.1016/J.CHROMA.2010.12.038

Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., and Mopper, K. (2008). Absorption spectral slopes and slope ratios as indicators of molecular weight, source and photobleaching of chromophoric dissolved organic matter. *Limnology and Oceanography* **53**, 955–969. doi:10.4319/LO.2008.53.3.0955

Hernes, P. J., and Benner, R. (2003). Photochemical and microbial degradation of dissolved lignin phenols: implications for the fate of terrigenous dissolved organic matter in marine environments. *Journal of Geophysical Research – Oceans* **108**, 3291. doi:10.1029/2002JC001421

Hood, E., Williams, M. W., and McKnight, D. M. (2005). Sources of dissolved organic matter (DOM) in a Rocky Mountain stream using chemical fractionation and stable isotopes. *Biogeochemistry* **74**(2), 231–255. doi:10.1007/S10533-004-4322-5

Hosen, J. D., McDonough, O. T., Febria, C. M., and Palmer, M. A. (2014). Dissolved organic matter quality and bioavailability changes across an urbanization gradient in headwater streams. *Environmental Science & Technology* **48**, 7817–7824. doi:10.1021/ES501422Z

Huang, W., McDowell, W. H., Zou, X., Ruan, H., Wang, J., and Ma, Z. (2015). Qualitative differences in headwater stream dissolved organic matter and riparian water-extractable soil organic matter under four different vegetation types along an altitudinal gradient in the Wuyi Mountains of China. *Applied Geochemistry* **52**, 67–75. doi:10.1016/J.APGEOCHEM.2014.11.014

Huguet, A., Vacher, L., Relexans, S., Saubusse, S., Froidefond, J. M., and Parlanti, E. (2009). Properties of fluorescent dissolved organic matter in the Gironde Estuary. *Organic Geochemistry* **40**, 706–719. doi:10.1016/J.ORGGEOCHEM.2009.03.002

Iriondo, M. (1989). Quaternary lakes of Argentina. *Palaeogeography, Palaeoclimatology, Palaeoecology* **70**, 81–88. doi:10.1016/0031-0182(89)90081-3

Jaffé, R., McKnight, D., Maie, N., Cory, R., McDowell, W. H., and Campbell, J. L. (2008). Spatial and temporal variations in DOM composition in ecosystems: the importance of long-term monitoring of optical properties. *Journal of Geophysical Research – Biogeosciences* **113**(G4), G04032. doi:10.1029/2008JG000683

Jaffé, R., Yamashita, Y., Maie, N., Cooper, W. T., Dittmar, T., Dodds, W. K., Jones, J. B., Myoshi, T., Ortiz-Zayas, J. R., Podgorskie, D. C., and Watanabe, A. (2012). Dissolved organic matter in headwater streams: compositional variability across climatic regions of North America. *Geochimica et Cosmochimica Acta* **94**, 95–108. doi:10.1016/J.GCA.2012.06.031

Jansson, M., Berggren, M., Laudon, H., and Jonsson, A. (2012). Bioavailable phosphorus in humic headwater streams in boreal Sweden. *Limnology and Oceanography* **57**, 1161–1170. doi:10.4319/LO.2012.57.4.1161

Jones, D. L., Healey, J. R., Willett, V. B., Farrar, J. F., and Hodge, A. (2005). Dissolved organic nitrogen uptake by plants – an important N uptake pathway? *Soil Biology & Biochemistry* **37**, 413–423. doi:10.1016/J.SOILBIO.2004.08.008

Korak, J. A., Wert, E. C., and Rosario-Ortiz, F. L. (2015). Evaluating fluorescence spectroscopy as a tool to characterize cyanobacteria intracellular organic matter upon simulated release and oxidation in natural water. *Water Research* **68**, 432–443. doi:10.1016/J.WATRES.2014.09.046

Larson, J. H., Frost, P. C., Xenopoulos, M. A., Williams, C. J., Morales-Williams, A. M., Vallazza, J. M., Nelson, J. C., and Richardson, W. B. (2014). Relationships between land cover and dissolved organic matter change along the river to lake transition. *Ecosystems* **17**(8), 1413–1425. doi:10.1007/S10021-014-9804-2

Laudon, H., Berggren, M., Ågren, A., Buffam, I., Bishop, K., Grabs, T., Jansson, M., and Köhler, S. (2011). Patterns and dynamics of dissolved organic carbon (DOC) in boreal streams: the role of processes, connectivity, and scaling. *Ecosystems* **14**(6), 880–893. doi:10.1007/S10021-011-9452-8

McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T., and Andersen, D. T. (2001). Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography* **46**(1), 38–48. doi:10.4319/LO.2001.46.1.0038

Messetta, M. L., Hegoburu, C., Casas-Ruiz, J. P., Butturini, A., and Feijoó, C. (2018). Characterization and qualitative changes in DOM chemical characteristics related to hydrologic conditions in a Pampean stream. *Hydrobiologia* **808**(1), 201–217. doi:10.1007/S10750-017-3422-X

Miller, M. P., and McKnight, D. M. (2010). Comparison of seasonal changes in fluorescent dissolved organic matter among aquatic lake and stream sites in the Green Lakes Valley. *Journal of Geophysical Research. Biogeosciences* **115**, G00F12. doi:10.1029/2009JG000985

Mostofa, K. M., Yoshioka, T., Konohira, E., and Tanoue, E. (2007). Photodegradation of fluorescent dissolved organic matter in river waters. *Geochemical Journal* **41**(5), 323–331. doi:10.2343/GEOCHEMJ.41.323

Nilsson, M., Sagerfors, J., Buffam, I., Laudon, H., Eriksson, T., Grelle, A., Klemedtsson, E., Weslien, P., and Lindroth, A. (2008). Contemporary carbon accumulation in a boreal oligotrophic minerogenic mire – a significant sink after accounting for all C-fluxes. *Global Change Biology* **14**, 2317–2332. doi:10.1111/J.1365-2486.2008.01654.X

Ohno, T. (2002). Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter. *Environmental Science & Technology* **36**(4), 742–746. doi:10.1021/ES0155276

Parlanti, E., Wörz, K., Geoffroy, L., and Lamotte, M. (2000). Dissolved organic matter fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs. *Organic Geochemistry* **31**(12), 1765–1781. doi:10.1016/S0146-6380(00)00124-8

Paruelo, J. M., Beltrán, A., Jobággy, E., Sala, O. E., and Golluscio, R. A. (1998). The climate of Patagonia: general patterns and controls on biotic processes. *Ecología Austral* **8**, 85–101.

Pérez, G. L., Torremorell, A., Bustingorry, J., Escaray, R., Pérez, P., Diéguez, M., and Zagarese, H. (2010). Optical characteristics of shallow lakes from the Pampa and Patagonia regions of Argentina. *Limnologica – Ecology and Management of Inland Waters* **40**(1), 30–39. doi:10.1016/J.LIMNO.2008.08.003

Peter, S., Shen, Y., Kaiser, K., Benner, R., and Durisch-Kaiser, E. (2012). Bioavailability and diagenetic state of dissolved organic matter in riparian groundwater. *Journal of Geophysical Research – Biogeosciences* **117**, G04006.

Peuravuori, J., and Pihlaja, K. (1997). Molecular size distribution and spectroscopic properties of aquatic humic substances. *Analytica Chimica Acta* **337**(2), 133–149. doi:10.1016/S0003-2670(96)00412-6

Queimaliños, C. P., Reissig, R., Diéguez, M. C., Arcagni, M., Ribeiro Guevara, S., Campbell, L., Soto Cárdenas, C., Rapacioli, R. A., and Arribére, M. (2012). Influence of precipitation, landscape and hydrogeomorphic lake features on pelagic allochthonous indicators in two connected ultraoligotrophic lakes of North Patagonia. *The Science of the Total Environment* **427–428**, 219–228. doi:10.1016/J.SCITOTENV.2012.03.085

Rapacioli, R. A. (2011). Caracterización hidrológica de la Reserva Natural Urbana Lago Morenito –Laguna Ezquerra. In 'Proyecto de Manejo de Reserva Natural Morenito-Ezquerra'. (Ed. A. Abalerón.) pp. 1–38. (Fundación Bariloche: Bariloche, Argentina.)

Rodrigues Capítulo, A., Gómez, N., Giorgi, A., and Feijoó, C. (2010). Global changes in Pampean lowland streams (Argentina): implications for biodiversity and functioning. *Hydrobiologia* **657**(1), 53–70. doi:10.1007/S10750-010-0319-3

Seitzinger, S. P., and Sanders, R. W. (1997). Contribution of dissolved organic nitrogen from rivers to estuarine eutrophication. *Marine Ecology Progress Series* **159**, 1–12. doi:10.3354/MEPS159001

Soto Cárdenas, C., Gerea, M., Garcia, P. E., Pérez, G. L., Diéguez, M. C., Rapacioli, R. A., Reissig, M., and Queimaliños, C. (2017). Interplay between climate and hydrogeomorphic features and their effect on the seasonal variation of dissolved organic matter in shallow temperate lakes of the Southern Andes (Patagonia, Argentina): a field study based on optical properties. *Ecohydrology* **10**, e1872. doi:10.1002/ECO.1872

Spencer, R. G. M., Baker, A., Ahad, J. M. E., Cowie, G. L., Ganeshram, R., Upstill-Goddard, R. C., and Uher, G. (2007). Discriminatory classification of natural and anthropogenic waters in two UK estuaries. *The Science of the Total Environment* **373**, 305–323. doi:10.1016/J.SCITOTENV.2006.10.052

Spencer, R. G. M., Hernes, P. J., Ruf, R., Baker, A., Dyda, R. Y., Stubbins, A., and Six, J. (2010). Temporal controls on dissolved organic matter and lignin biogeochemistry in a pristine tropical river, Democratic Republic of Congo. *Journal of Geophysical Research – Biogeosciences* **115**, G03013. doi:10.1029/2009JG001180

Spencer, R. G. M., Butler, K. D., and Aiken, G. R. (2012). Dissolved organic matter and chromophoric dissolved organic matter properties of rivers in the USA. *Journal of Geophysical Research – Biogeosciences* **117**, G03001.

Stanley, E. H., Powers, S. M., Lottig, N. R., Buffam, I., and Crawford, J. T. (2012). Contemporary changes in dissolved organic carbon (DOC) in human-dominated rivers: is there a role for DOC management? *Freshwater Biology* **57**, 26–42. doi:10.1111/J.1365-2427.2011.02613.X

Stedmon, C. A., and Cory, R. M. (2014). Biological origins and fate of fluorescent dissolved organic matter in aquatic environments. In 'Aquatic Organic Matter Fluorescence'. (Eds P. Coble, J. Lead, A. Baker, D. Reynolds, and R. G. M. Spencer.) pp. 278–299. (Cambridge University Press: New York, NY, USA.)

Vilches, C., and Giorgi, A. (2010). Metabolism in a macrophyte-rich stream exposed to flooding. *Hydrobiologia* **654**(1), 57–65. doi:10.1007/S10750-010-0368-7

Walker, S. A., Amon, R. M., and Stedmon, C. A. (2013). Variations in high-latitude riverine fluorescent dissolved organic matter: a comparison of large Arctic rivers. *Journal of Geophysical Research – Biogeosciences* **118**(4), 1689–1702. doi:10.1002/2013JG002320

Watanabe, A., Moroi, K., Sato, H., Tsutsuki, K., Maie, N., Melling, L., and Jaffé, R. (2012). Contributions of humic substances to the dissolved organic carbon pool in wetlands from different climates. *Chemosphere* **88**(10), 1265–1268. doi:10.1016/J.CHEMOSPHERE.2012.04.005

Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., and Mopper, K. (2003). Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental Science & Technology* **37**(20), 4702–4708. doi:10.1021/ES030360X

Williams, C. J., Yamashita, Y., Wilson, H. F., Jaffé, R., and Xenopoulos, M. A. (2010). Unraveling the role of land use and microbial activity in shaping dissolved organic matter characteristics in stream ecosystems. *Limnology and Oceanography* **55**(3), 1159–1171. doi:10.4319/LO.2010.55.3.1159

Wilson, H. F., and Xenopoulos, M. A. (2009). Effects of agricultural land use on the composition of fluvial dissolved organic matter. *Nature Geoscience* **2**(1), 37–41. doi:10.1038/NGEO391

Yates, C. A., Johnes, P. J., and Spencer, R. G. M. (2016). Assessing the drivers of dissolved organic matter export from two contrasting lowland catchments, UK. *The Science of the Total Environment* **569–570**, 1330–1340. doi:10.1016/J.SCITOTENV.2016.06.211

Zagarese, H. E., Diaz, M., Pedrozo, F., Ferraro, M., Cravero, W., and Tartarotti, B. (2001). Photodegradation of natural organic matter exposed to fluctuating levels of solar radiation. *Journal of Photochemistry and Photobiology – B. Biology* **61**, 35–45. doi:10.1016/S1011-1344(01)00142-7

Zhang, Y., Liu, X., Wang, M., and Qin, B. (2013). Compositional differences of chromophoric dissolved organic matter derived from phytoplankton and macrophytes. *Organic Geochemistry* **55**, 26–37. doi:10.1016/J.ORGGEOCHEM.2012.11.007

Zsolnay, A., Baigar, E., Jimenez, M., Steinweg, B., and Saccomandi, F. (1999). Differentiating with fluorescence spectroscopy the sources of dissolved organic matter in soils subjected to drying. *Chemosphere* **38**(1), 45–50. doi:10.1016/S0045-6535(98)00166-0

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