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Landscape integration of North Patagonian mountain lakes: a first approach using characterization of dissolved organic matter

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Abstract

North-western Patagonia contains a variety of glacially formed mountain lakes located at different positions from the treeline in the Andean Patagonian forest region. Water chemistry of six North Patagonian lakes located in an altitudinal gradient, above, at and below the treeline (~41°S) were analysed in this study. The relative importance of allochtonous to autochthonous carbon inputs along a marked catchment vegetation gradient encompassing altoandino vegetation and *Nothofagus* forests was addressed. The dissolved organic carbon (DOC) concentration varied among the study lakes, with the lakes located higher in the landscape exhibiting lower DOC concentrations (<1 mg L^{-1}) than lakes located at or below the treeline (>2 mg L^{-1}). Analysis of coloured and fluorescent dissolved organic matter (CDOM and FDOM, respectively) followed the DOC pattern, despite the contrasting catchments of the study lakes. The results indicated the CDOM in all the lakes had low molecular weight and low aromaticity. The excitation–emission matrices (EEMs) highlighted three distinctive fluorophores in the FDOM, including two humic-like (peak A and peak C) revealing the presence of humic terrestrial material, and a protein-like fluorophore (peak T) generally associated with autochthonous DOM. The increased intensities of the humic fluorophores in the lakes located below the treeline suggest higher allochtonous carbon inputs from their catchments. This evidence collectively suggests that mountain lakes exhibit some heterogeneity in terms of DOM, likely attributable to their position in relation to the treeline, which determines the contribution of the catchment. As remote lakes are extremely sensitive to changes in their catchments, these North Patagonian mountain lakes may accurately track the impact of climate and anthropogenic changes on the landscape.

Key words

dissolved organic matter, fluorescence excitation–emission matrix (EEM), mountain lakes, water chemistry.

INTRODUCTION

Analysis of the dissolved organic matter (DOM) character of aquatic systems is crucial for better understanding the influence of the terrestrial surroundings on the systems. Study of the spectral properties of the chromophoric DOM (CDOM) and its fluorescent fraction (FDOM) can provide valuable information about these kinds of interactions, thereby allowing a comprehensive characterization of the DOM pool (Mcknight *et al.* 2001; Coble 2007; Helms *et al.*2008; Chen *et al.* 2011). In particular, spatial and temporal dynamics of DOM have been studied on the basis of either UV-visible absorption (associated with CDOM) (Del Vecchio & Blough 2004; Helms *et al.*2008; Spencer *et al.* 2008; Loiselle *et al.* 2009) or fluorescence (associated with FDOM) (Baker & Spencer 2004; Murphy *et al.* 2008; Kowalczuk *et al.* 2009; Zhang *et al.* 2009), highlighting the importance of spectral analyses in environmental surveys.

Lakes can be viewed as patches organized in a complex terrestrial and aquatic matrix, in which human influences also interact at multiple spatial scales. This perspective is useful for understanding the spatial heterogeneity across lakes within an ecoregion and/or a lake district (Kratz *et al.* 1997; Soranno *et al.* 2009). The position of a lake in a flow system influences the relative hydrologic balance between precipitation, groundwater and surface water inputs. A lake located high in the landscape, for example, receives most of its water from atmospheric deposition (i.e. precipitation/snow), whereas a lake located low in the

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landscape receives a substantial input from superficial inlets and/or the groundwater network (Webster *et al.* 2000; Kratz *et al.* 2006). Lakes located higher in the landscape are smaller, chemically more diluted, more transparent, used less by humans than lakes located lower in the flow system (Riera *et al.* 2000; Kratz *et al.* 2006). Mountain lakes are good examples of ‘high lakes’, typically being characterized by nutrient and DOM concentrations determined by a small input of allochtonous materials, as well as autochthonous productivity (Williamson *et al.* 2009; Mladenov *et al.* 2011; De Laurentiis *et al.* 2012). DOM and nutrient concentrations are particularly influenced by geology, catchment vegetation, precipitation patterns and atmospheric deposition (Marchetto *et al.* 1995; Kamenik *et al.* 2001; Webster *et al.* 2008; De Laurentiis *et al.* 2012). High-altitude lakes located at different sites across the treeline with catchments dominated either by rocks, meadows or forests are differentially affected by the terrestrial environment. There also is increasing evidence supporting the idea that polar and alpine lakes are undergoing rapid climate change and are being considered as the most sensitive sentinels of this global process (Adrian *et al.* 2009; Williamson *et al.* 2009). To this end, optical changes in the UV region and fluorescence in mountain lake waters are effective sentinels of such global change processes as atmospheric transport and deposition (Mladenov *et al.*2009, 2011).

North-western Patagonia contains a great variety of glacially formed lakes, typically located above 750 m.a.s.l. in the Andes (Thomasson 1959; Quirós & Drago 1999; Zagarese *et al.* 2000). The trophic status of these mountain lakes ranges from ultra-oligotrophic to mesotrophic (Morris *et al.* 1995; Zagarese *et al.* 2000; Diaz *et al.* 2007; Mladenov *et al.* 2011). As a result of the natural increase of the ultraviolet radiation (UVR) flux with elevation, mountain lakes are exposed to high solar radiation levels, particularly UVR. Moreover, light penetration in the water column is extremely high because of their typically low dissolved organic carbon (DOC) concentrations and their shallow depths (Zagarese *et al.* 1998, 2000; Diaz *et al.* 2006). Mountain lakes in this area occur below, at and/or above the treeline. At the altitudinal treeline, vegetation ranges from continuous forests of *Nothofagus pumilio* erect trees to grass-dominated altoandino vegetation, with a transitional ecotone in which *N. pumilio* trees with erect and *krummholz* (shrubby-shaped) growth forms occur. Upslope from the timberline, the tree density decreases, and the forest cover becomes less continuous as the *krummholz* forest transitions into altoandino vegetation. The location of the uppermost *krummholz* tree determines the treeline position of the treeline. The treelines in the Southern Hemisphere reflect the sustained climate changes (i.e. drying and warming observed at mid-latitudes because of stratospheric ozone depletion) experienced in the region during the past 4–5 decades (Daniels & Veblen 2003; Villalba *et al.* 2012).

Analysis of carbon loads and exchange within a catchment including terrestrial and aquatic systems appears as an appropriate and accurate approach to better understand the influence of climate change at the landscape level. Lakes integrate information about changes in their catchment (Adrian *et al.* 2009 and references therein). Lake chemistry reflects processes occurring in the surrounding terrestrial landscape, with local nutrient concentrations being altered by changes in their terrestrial export related to climatic influences on weathering rates, precipitation, run-off or terrestrial primary productivity.

This study examines the water chemistry parameters of six mountain lakes in North Patagonia (~41°S) located at different position in the landscape, encompassing systems located above, at and below the treeline. A first environmental survey of the relative contribution of the catchment to lakes was performed, through the combination of dissolved organic carbon (DOC) measurements and assessment of the spectral properties of CDOM and its fluorescent fraction (FDOM). It is expected that lakes located higher in the landscape (i.e. above the treeline) will contain lower DOC concentrations than lakes located lower in the landscape. This study also predicts differences in the DOM quality of these mountain lakes along the altitudinal gradient, reflecting heterogeneity in their catchments.

MATERIAL AND METHODS

Study sites

This study included 6 mountain lakes located along an altitudinal gradient (866–1940 m.a.s.l.), and in a restricted latitudinal (41°10′S–41°23′S) and longitudinal (71°17′–71°49′W) range (Table 1; Fig. 1), all being in the Nahuel Huapi National Park (Northern Patagonia, Argentina). Following the ordination proposed by Daniels and Veblen (2003), two lakes are located above the treeline (lakes Schmoll and Témpanos) on a rocky substrate with scarce soil development, two lakes are located in the treeline ecotone (lakes Toncek and Jakob), and two are located at the timberline (lakes Verde and Juventus). Lakes Toncek and Schmoll are located in Mount Catedral, being neighbouring systems, with upper Lake Schmoll flowing down to Lake Toncek during the ice-free period. Lakes Témpanos and Jakob are located in Mount Navidad, with a similar hydrologic arrangement, with Lake Témpanos

Table 1. Location and morphometric parameters of study mountain lakes in North Patagonia (Argentina)

Lake	Location	Altitude (m.a.s.l)	Area (ha)	Depth (m)	Electrical conductivity (μS cm^{-1})	pH
Verde	41°15′03″S–71°17′06″W	1545	0.35	5	30.1	7.4
Juventus	41°23′04″S–71°31′05″W	1010	4.55	12	77.8	7.1
Toncek	41°11′04″S–71°29′17″W	1743	5.19	9	14.4	7.0
Jacob	41°12′00″S–71°34′01″W	1550	15.33	25	14.7	6.4
Tempanos	41°10′06″S–71°34′06″W	1650	9.53	5	6.8	6.7
Schmoll	41°11′03″S–71°30′00″W	1940	2.80	5	8.0	6.9

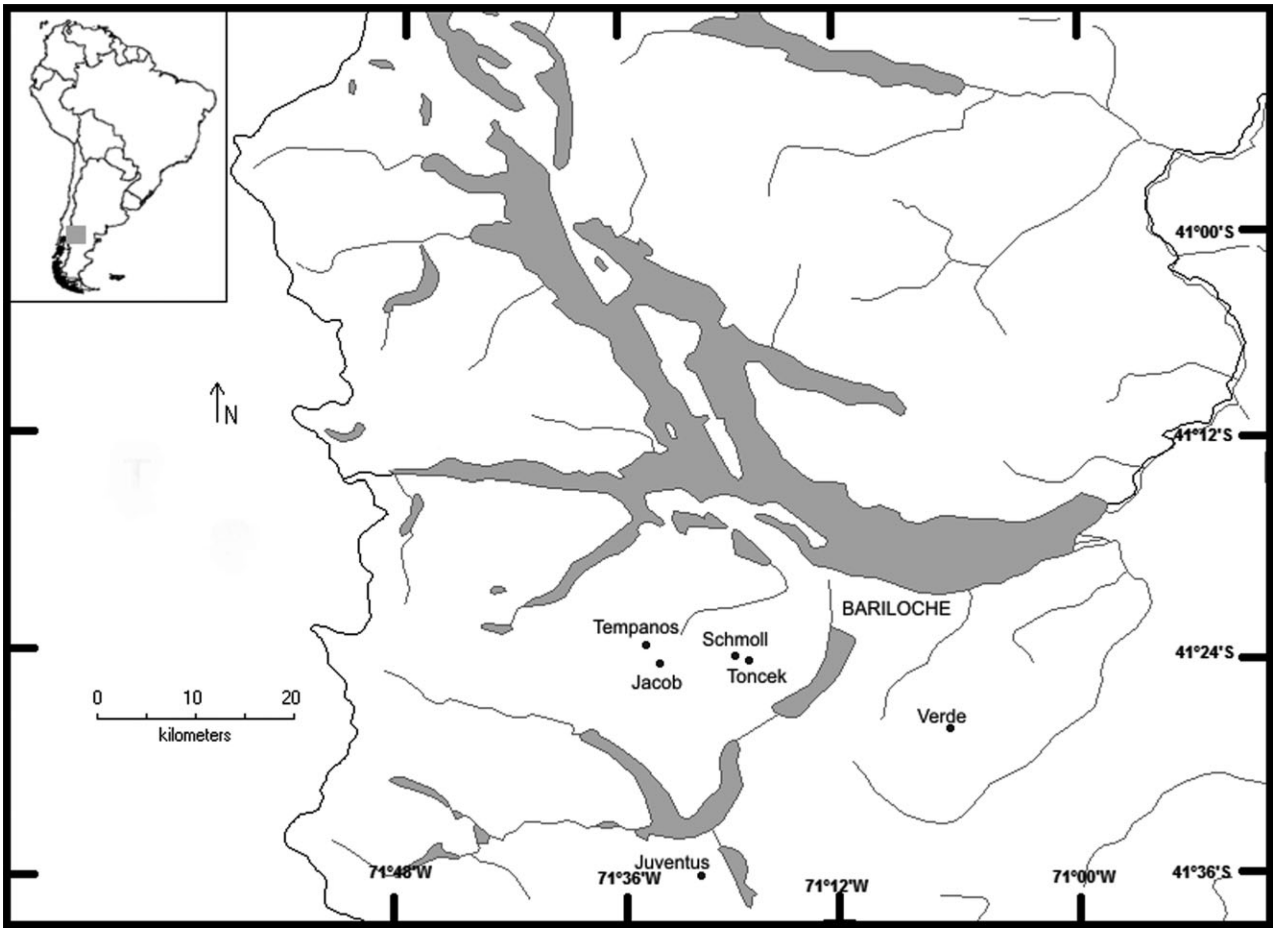

Fig. 1. Map of study area and six mountain lakes (North Patagonia, Argentina).

located higher in the flow system. The mountain lakes in both cases flow through permanent streams to large and deep piedmont lakes (Fig. 1). In contrast, Lake Verde is located on Mount Challhuaco (Ventana Formation) on a mountainous terrain characterized by sedimentary rocks and andesites with slopes and flooded meadows (Zagarese *et al.* 2000; Varela *et al.* 2005). Lake Juventus, the southernmost lake of the study regime, is located at the bottom of the valley of Padre Laguna Mount. Comparatively, the basement in this area is formed by coarse-grained metamorphic rocks (García-Sansegundo *et al.* 2009). The outlets of lakes Verde and Juventus are small and temporary.

The climate in this area is mainly temperate, with most of the annual precipitation occurring during autumn and winter (Barros *et al.* 1983; Daniels & Veblen 2003). The area precipitation records indicate that up to ~1500 mm of mean annual precipitation occurs, decreasing abruptly towards the east where the precipitation may be ~800 mm (Jobbágy *et al.* 1995; Paruelo *et al.*

1998; Daniels & Veblen 2003). The lakes are usually covered by ice and/or snow for 6 to 8 months each year (Zagarese *et al.* 2000). The vegetation surrounding the lakes above the treeline is flora typical of the high Andes (known as 'altoandino' vegetation), being characterized by perennial herbs and subshrubs. The vegetation below the treeline is characterized by a *Nothofagus* forest (Ferreyra *et al.* 1998; Daniels & Veblen 2003; Mermoz *et al.* 2009).

Lakes Verde, Témpanos and Schmoll are the shallowest lakes(<6 m depth), and lakes Juventus and Toncek have intermediate maximum depths (6–12 m), while Lake Jakob is the deepest system (25 m) (Table 1). According to previous studies, Lake Verde is considered mesotrophic, whereas lakes Toncek, Témpanos and Schmoll are ultra-oligotrophic (Zagarese *et al.* 2000; Diaz *et al.* 2007).

Sample collection and processing

Water samples were collected from the six mountain lakes from March to April 2013 during the ice-free period. Samples were obtained with a 4.5 L Kemmerer bottle at 3 different depths along the water column in the case of lakes Verde, Toncek and Juventus, and from the subsurface in the case of lakes Schmoll, Jakob and Témpanos. Each sample was transferred to 2 L polycarbonate carboys (acid-washed and rinsed with the water sampled at the beginning of sample collection). Electrical conductivity and pH were measured *in situ* using an YSI 85 probe.

Laboratory analyses

Whole water samples (1000 mL) collected from each site were separated for the analysis of total phosphorus (TP), total nitrogen (TN) and chlorophyll-*a* concentrations. The TP concentration was determined by digestion with persulfate at 1.5 atmospheres for 1 h, followed by the molybdate reaction, as described by APHA (2005). The TN concentrations were performed by oxidizing with persulfate and determining nitrate-N with second-derivative spectroscopy (Bachmann & Canfield 1996). The chlorophyll-*a* concentrations were assessed by filtering a volume of the water samples from each site through a preburned glass fibre filter (Whatman GF/F; 0.7 μm). The material retained in the filters was extracted with ethanol (90%), with the extracts being scanned with a UV-visible spectrophotometer (Hewlett–Packard 8453), according to Nusch (1980).

Dissolved organic carbon and dissolved organic matter characterization

The dissolved organic carbon concentrations were determined with a Shimadzu TOC-L high temperature analyser, measuring non-purgeable organic carbon. The mean of 3–5 injections of 400 μL was reported for each sample, with the precision described as the coefficient of variance (CV), which was <2% for the replicated injections. The reported values were corrected for the instrument blank measured concurrently.

The absorbance spectra (200–800 nm) from filtered water samples (Millipore, Sao Pablo, Brazil, PVDF membranes, 0.22 μm) were obtained at 1 nm intervals in a UV-visible spectrophotometer, using a 100 mm quartz cuvette. ASTM1 grade water (Milli-Q, Millipore inc. Molsheim, France) was used as reference blank. 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, following the procedure of Helms *et al.* (2008). All the absorbance data were converted to absorption coefficients as follows:

$$a = 2.303A/l \tag{1}$$

where: a = Napierian absorption coefficient (m^{-1}); A = absorbance; and l = path length (m).

The absorption coefficients were calculated as proxies of chromophoric DOM (CDOM) composition. In particular, the absorption at 350 nm (a_{350}) was associated with terrestrial CDOM, as previous investigations have demonstrated its positive relationship with lignin phenol concentrations (Hernes & Benner 2003; Spencer *et al.* 2008). The water colour was estimated, based on the absorbance at 440 nm (a_{440}), according to the procedure of Reche *et al.* (1999). The spectral slopes for the intervals 275–295 nm ($S_{275–295}$) and 350–400 nm ($S_{350–400}$), which were indicative of the molecular weight/size of the DOM, and the slope from 290–350 nm ($S_{290–350}$) used as a proxy of the DOM composition, were calculated by fitting the log-transformed spectral data to a linear regression. The resulting slopes were expressed as positive numbers, according to a mathematical convention (Helms *et al.* 2008). The slope ratio (S_R) was calculated as the ratio of $S_{275–295}$ to $S_{350–400}$, being used as a proxy of the relative molecular weight/size of the DOM (Helms *et al.* 2008). The specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) was calculated as the absorbance coefficient (m^{-1}) at 254 nm divided by DOC concentration (mg L^{-1}) (Table 2).

Additionally, the filtered water samples were scanned for the analysis of FDOM in a spectrofluorometer Perkin-Elmer 55B equipped with a 150-W Xenon arc lamp and a Peltier temperature controller, using a 1 cm quartz fluorescence cell. The raw excitation–emission matrices (EEMs) were collected at specific excitation wavelengths

Table 2. Definition and significance of optical and fluorescence dissolved organic matter characteristics in present study

DOM characterization	Formula	Definition	References
Absorbance-based			
Lignin compounds (a350)		Used as proxy for lignin	Hernes & Benner 2003
Water colour (a440)		Used as predictor of light attenuation	Reche *et al.* 1999
Spectral slope 275–295 nm ($S_{275–295}$)		Used to indicate DOM composition	Helms *et al.* 2008
Spectral slope 290–350 nm ($S_{290–350}$)		Sensitive to changes in DOM source and processing	Spencer *et al.* 2007
Spectral slope 350–400 nm ($S_{350–400}$)		Relative molecular weight/size of DOM	Helms *et al.* 2008
Slope eatio (S_R)	$S_{295–295}/S_{350–400}$	Can be used as proxy for molecular weight	Helms *et al.* 2008
Specific ultraviolet absorbance at 254 (SUVA)	a(254 nm)/ mg L^{-1}	Provides indication of aromaticity	Weishaar *et al.* 2003
Fluorescence-based			
Fluorescence index (FI)	I450/I500 at ex370 nm	DOM source (microbial or terrestrial)	Mcknight *et al.* 2001;
Humification index (HIX)	Σ435–480/(Σ300–345 + Σ435–480)	Used to characterize humification status	Ohno 2002
Freshness index (BIX)	I380 nm/max (I420–I435 nm)	Relative contribution of fresh DOM to recalcitrant DOM	Huguet *et al.* 2009; Wilson & Xenopoulos 2008

(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 prepared with 10 nm excitation and emission slits and a scan speed of 1500 nm min^{-1}. The EEMs were processed with the software FL–WinLab® (Perkin-Elmer, Shelton, CT, USA). Absorbance spectra (200–800 nm) were used to develop a matrix of correction factors for each fluorescence EEM, using the Matlab toolbox FDOMcorr, and 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 were expressed in Raman units (Murphy *et al.* 2010).

Three fluorescent DOM indicators were calculated. The fluorescence index (FI) was extracted from the corrected EEMs as the ratio of the emissions at 470 to 520 nm excited at 370 nm, according to the procedure of Cory *et al.* (2010). The humification index (HIX) was calculated as the sum of the emission between 435 and 480 nm, divided by the sum of the emission range between 300 and 345 nm, at the excitation 255 nm, corrected after the procedure of Ohno (2002). The index of recent autochthonous contribution [BIX or freshness index (β/α)] was calculated as the ratio of the emission intensity at 380 nm, divided by the maximum emission intensity between 420 and 435 nm, at excitation 310 nm (Table 2).

Data analyses

Vegetation cover percentages were determined along each lake perimeter using satellite images. These data represent only local land cover, as catchment boundaries are not available for the studied lakes.

Basic descriptive statistics (mean and standard deviation) were used to describe the absorbance and fluorescence values. Correlation analysis (Pearson correlation) was applied to study the relationship between chemical parameters in the environmental gradient. Data were analysed for distribution and homoscedasticity using the normality and equal variance tests. All data analyses were performed using Sigma Plot 9.0 with the Sigma Stat 3.5 package, Systat software inc, San Jose, CA, USA.

A principal component analysis (PCA) was performed, using 15 variables (altitude, percentage (%) vegetation, electrical conductivity, total phosphorus concentration (TP), total nitrogen concentration (TN), chlorophyll-*a* concentration, dissolved organic carbon concentration (DOC), specific UV absorbance (SUVA), slope ratio (SR), freshness index (BIX), peak A, peak C, peak T, a_{254} and a_{440}). The PCA was carried out using the software STATISTICA (version 6.0) Statsoft inc, Tulsa, OK, USA.

RESULTS AND DISCUSSION

Water chemistry

The electrical conductivity ranged from extremely low (<10 μS cm^{-1}) values for lakes Témpanos and Schmoll, to slightly higher values (10–50 μS cm^{-1}) in lakes Jakob, Toncek and Verde. The highest conductivity was recorded for Lake Juventus (78 μS cm^{-1}). The conductivity of the lakes generally decreased significantly with increasing altitude ($r = -0.92$, $p = 0.008$). This pattern may be attributable to the larger contribution of calcium from the catchment and underground water in lakes lower in the landscape (Kratz *et al.* 1997). The pH varied around neutral in the set of lakes. Lakes Schmoll, Témpanos, Toncek and Jakob, however, exhibited a slightly acidic to neutral pH, while lakes Verde and Juventus exhibited slightly higher pH values (Table 1).

The DOC concentrations varied between 0.4 and 3.2 mg L^{-1} among the study lakes. The DOC concentration was highest for Lake Verde (~3 mg L^{-1}), followed by Lake Juventus (~2 mg L^{-1}), with a concentration <1 mg L^{-1} measured for the remaining lakes (Fig 2a). These DOC concentrations are extremely low, indicating the clear water condition of these pristine environments was previously stressed out (Zagarese *et al.* 2000; Mladenov *et al.* 2008; Rose *et al.* 2009). Concomitantly, the total nitrogen (TN) and phosphorus (TP) concentrations were very low. The highest TP and TN concentrations were recorded for Lake Verde (14.13 ± 3.66 and 470 ± 38 μg L^{-1}, respectively), while the lowest concentrations were recorded for lakes Toncek (TP = 8.03 ± 1.88 μg L^{-1} and TN = 175.8 ± 29.4 μg L^{-1}) and Témpanos (TP = 5.77 μg L^{-1} and TN = 88.6 μg L^{-1}) (Fig. 2b,c). A wide range in the chlorophyll-*a* concentration was observed among the studied lakes. The highest values were recorded for Lake Verde (5.62 ± 2.17 μg L^{-1}), followed by Lake Toncek (1.33 ± 0.18 μg L^{-1}). The chlorophyll-*a* concentrations were <1 μg L^{-1} in the remaining study lakes (Fig. 2d).

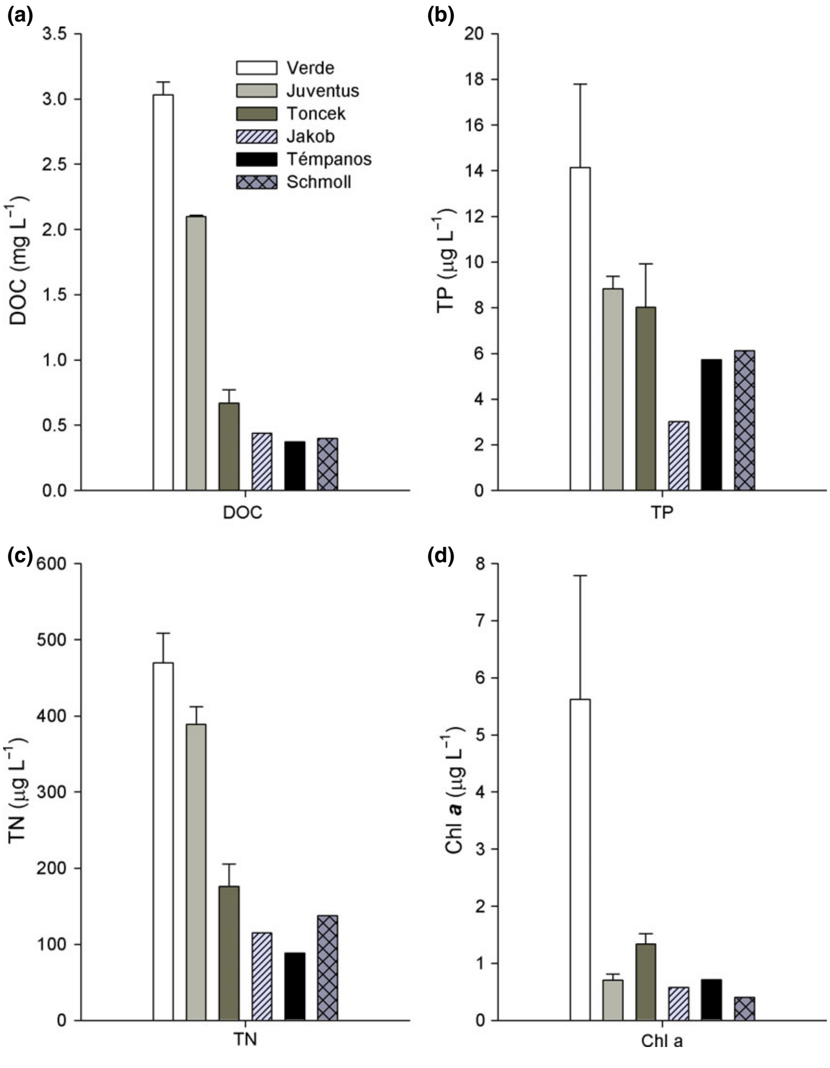

Fig. 2. Water chemistry characteristics of six mountain lakes in North Patagonia, Argentina (a = dissolved organic carbon (DOC) concentration; b = total phosphorous (TP) concentration; c = total nitrogen (TN) concentration; d = chlorophyll-*a* concentration).

The TP and TN concentrations were directly correlated with the DOC concentration ($r = 0.89$ and $r = 0.99$, $p < 0.05$, respectively), suggesting these nutrients have the same source as the DOC, a pattern also previously reported by Williamson *et al.* 1999 and Webster *et al.* (2008). As expected, the chlorophyll-*a* concentration was significantly correlated with TP ($r = 0.84$, $p < 0.05$).

The comparatively higher DOC, nutrient and chlorophyll-*a* concentrations measured for Lake Verde revealed its mesotrophic state, in agreement with previous investigations (Diaz *et al.* 1994, 2007; Zagarese *et al.* 2000). It is suggested this higher trophic condition could be attributed to the geological features of its catchment, considering its location on marine sedimentites (Pereyra 2007), which probably release phosphorous compounds. Lake Juventus exhibited intermediate DOC, TN and TP values, although low chlorophyll-*a* concentrations reflected its oligotrophic condition. The very low DOC, nutrient and chlorophyll-*a* concentrations measured for lakes Toncek, Schmoll, Jakob and Témpanos highlight their ultra-oligotrophic condition (Fig. 2a–d). The particular trophic conditions and clear water status of these latter lakes were reported in previous studies (Morris *et al.* 1995; Zagarese *et al.* 2000; Rose *et al.* 2009; Peréz *et al.* 2010; Mladenov *et al.* 2011).

DOM characterization

Coloured dissolved organic matter (CDOM)

The absorption scans of the natural lake water showed an increasing gradient from lakes Schmoll, Témpanos, Jakob, Toncek and Juventus to Lake Verde. The highest absorption values were recorded in the UV region for all the lakes, although being variable among the lakes. Above 400 nm more similarity among lakes was observed, although Lake Verde had higher absorbance values (Table 3, Fig. 3).

The absorbance-based DOM characterization, which included three absorption coefficients, exhibited a range of values of these parameters from extremely low to low. The absorption coefficients a_{254} and a_{350} exhibited higher values in lakes Verde and Juventus, and comparatively lower values in lakes Toncek, Jakob Témpanos and Schmoll (Table 3). In contrast, lakes Schmoll and Témpanos exhibited the lowest coefficient values, matching their lowest DOC concentration. The highest values of a_{350} particular would indicate higher lignin phenol concentrations (Hernes & Benner 2003; Spencer *et al.* 2008, 2009). The coefficient $a_{440,}$ indicative of water colour and associated with allochtonous DOM inputs (Rasmussen *et al.* 1989), indicated higher values for lakes Verde and Juventus (>0.17 m^{-1}), being lower in Toncek, Témpanos, Jakob and Schmoll (<0.17 m^{-1}). These results collectively indicated a relatively higher DOC concentration in lakes Verde and Juventus, compared to the other lakes. Positive correlations were found between the DOC concentration and the a_{254} ($r = 0.95$, $p < 0.05$), a_{350} ($r = 0.95$, $p < 0.05$) and a_{440} ($r = 0.90$, $p < 0.05$). Such trends have been reported in previous studies, supporting the idea that these coefficients can be applied as proxies of DOC concentrations (Spencer *et al.* 2008, 2009).

The specific UV absorbance, $SUVA_{254,}$ indicated lowest results for Lake Schmoll (1.14 L mg^{-1} m^{-1}), followed by Témpanos, Jakob and Verde (~2 L mg^{-1} m^{-1}). The highest $SUVA_{254}$ values were registered for lakes Toncek and Juventus (~3 L mg^{-1} m^{-1}) (Table 3). Overall, the $SUVA_{254}$ range results revealed the lakes were within a gradient regarding the contribution of the surrounding environment. The input of allochtonous DOM to aquatic ecosystems is associated with basin soil development (Williamson *et al.* 2009). Thus, the DOM for Témpanos and Schmoll, which are located in rocky terrains devoid of vegetation, exhibited negligible signs of terrestrial carbon inputs. In contrast, the DOM in lakes Verde and Juventus exhibit terrestrial signals, likely a contribution from their forested catchments. The $SUVA_{254}$ has been used as an indicator of the aromaticity of the DOM, with higher $SUVA_{254}$ thereby implying a higher aromaticity, and suggesting a supply of terrestrial DOM (Weishaar *et al.* 2003; Spencer *et al.* 2008).

The spectral slope $S_{275–295}$ calculated for all lakes indicated values between 15 and 25 × 10^{-3} $nm^{-1.}$ The lowest slope, $S_{275–295}$, was observed for Lake Témpanos, increasing as one moved towards lakes Toncek, Jakob, Schmoll, Verde and Juventus. Overall, the low $S_{275–295}$ values recorded for all these lakes are indicative of the predominance of low molecular weight material in the DOM, being within the range reported in previous investigations for Andean and Alpine lakes (Mladenov *et al.* 2011), and comparatively lower than the slopes recorded for piedmont Andean lakes in the same area (Diéguez *et al.* 2013). The slope $S_{290–350}$ exhibited a similar pattern than the $S_{275–295}$ slope, reflecting the dominance of low molecular weight DOM (Table 3) (Hernes *et al.* 2008; Spencer *et al.* 2008). Similarly, the slope $S_{350–400}$ decreased from lakes Verde and Juventus, and moving towards Toncek, Jakob, Témpanos and Schmoll. Steeper slopes have been interpreted as corresponding to low molecular weight DOM, while shallower slopes indicate a comparatively higher aromatic content and molecular weight (Table 3) (Helms *et al.* 2008; Spencer *et al.* 2009; De Laurentiis *et al.* 2012; Fleck *et al.* 2013).

Table 3. Catchment and vegetation features of six study mountain lakes (North Patagonia, Argentina) and characterization of dissolved organic matter

	Lake Verde	Lake Juventus	Lake Toncek	Lake Jakob	Lake Témpanos	Lake Schmoll
Catchment features						
Surrounding vegetation cover (%)	81.2	100	34.7	88.0	0	0
Type	T	T	TM	TM	R	R
Absorbance-based parameters						
a_{254} (m^{-1})	6.10 ± 0.95	6.30 ± 0.39	2.07 ± 0.09	1.04 ± 0.01	0.84	0.46
a_{350} (m^{-1})	0.99 ± 0.64	0.96 ± 0.24	0.47 ± 0.06	0.24 ± 0.032	0.291	0.13
a_{440} (m^{-1})	0.22 ± 0.37	0.17 ± 0.13	0.15 ± 0.06	0.09 ± 0.02	0.135	0.09
$S_{275–295}$ ($\times 10^{-3}$ nm^{-1})	23 ± 2	25 ± 1	20 ± 1	21 ± 0.9	15	23
$S_{290–350}$ ($\times 10^{-3}$ nm^{-1})	22 ± 6	20 ± 2	16 ± 1	14 ± 0.5	8	11
$S_{350–400}$ ($\times 10^{-3}$ nm^{-1})	35 ± 20	21 ± 4	14 ± 2	11 ± 3	8.9	7
S_R	0.91 ± 0.62	1.22 ± 0.22	1.46 ± 0.27	1.89 ± 0.51	1.69	3.31
$SUVA_{254}$ (L mg^{-1} m^{-1})	2.02 ± 0.37	3.03 ± 0.14	3.11 ± 0.37	2.27	2.28	1.15
Fluorescence-based parameters						
Humification (HIX)	0.75 ± 0.04	0.82 ± 0.002	0.74 ± 0.07	0.73 ± 0.009	0.72	1.06
Index of recent contribution (BIX)	0.72 ± 0.03	0.73 ± 0.002	0.73 ± 0.01	0.68 ± 0.01	0.54	0.78

Absorbance CDOM coefficients and fluorescence FDOM indexes; T = Forest; R = Rocky; TM = Forest and herbaceous meadows.

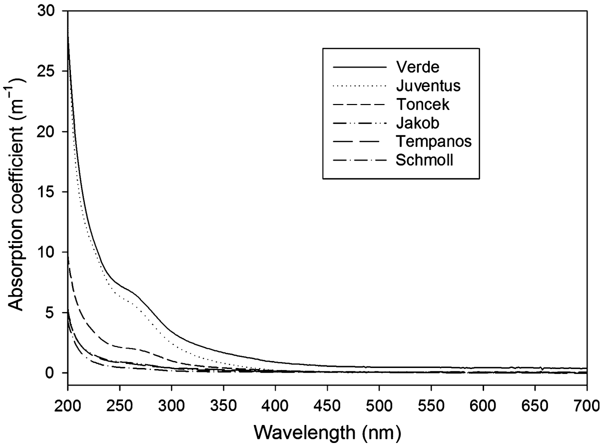

Fig. 3. Absorption spectra of water of six study mountain lakes (North Patagonia, Argentina).

The slope ratio S_R ($S_{275–295}$:$S_{350–400}$) was highest for Lake Schmoll (3.3). The other lakes exhibited comparatively lower values (<2), increasing steadily from Lake Verde as one moves towards lakes Juventus, Toncek, Témpanos, Jakob and Schmoll. The relatively high S_R found for Lake Schmoll indicated a low DOM input from the catchment, reflecting a lack of vegetation, a low contribution from the granite basement weathering and a low atmospheric deposition (Mladenov *et al.* 2011). The DOC concentration and CDOM level (as described by the a_{254}) are extremely low for Lake Schmoll, similar to other high-altitude lakes around the world (Reche *et al.* 2001; Sommaruga & Augustin 2006; Mladenov *et al.* 2008, 2011). Such low S_R values are usually found in highly diluted environments, such as marine coastal water (Helms *et al.* 2008). In contrast, lakes Verde and Juventus have comparatively lower S_R values, reflecting an increased DOM input from the surrounding forest, run-off and groundwater (Table 3).

Fluorescent dissolved organic matter (FDOM)

A first characterization of FDOM was assessed via calculating the corrected fluorescence index (FI), which is widely used as an indicator of the origin of the FDOM (Cory *et al.* 2010; Mladenov *et al.* 2011; De Laurentiis *et al.* 2012). In very diluted water such as Andean mountain lakes, however, the FI fails to highlight differences, likely due to a lack of fluorescence in the spectral region of 470–520 nm, at an excitation of 370 nm (Fig. 4a–f).

The humification index (HIX) indicated a decrease of DOM humification from Lake Juventus as one moved towards lakes Verde, Toncek, Jakob and Témpanos (Table 3). The lack of fluorescence in the sample from Lake Schmoll (Fig. 4f) did not allow for calculation of the HIX. The freshness index (BIX) exhibited the lowest value for Lake Témpanos, followed by lakes Jakob, Verde, Toncek, Juventus and Schmoll (Table 3). The BIX of the six lakes ranged between 0.54 and 0.78. According to Wilson and Xenopoulos (2008), BIX values between

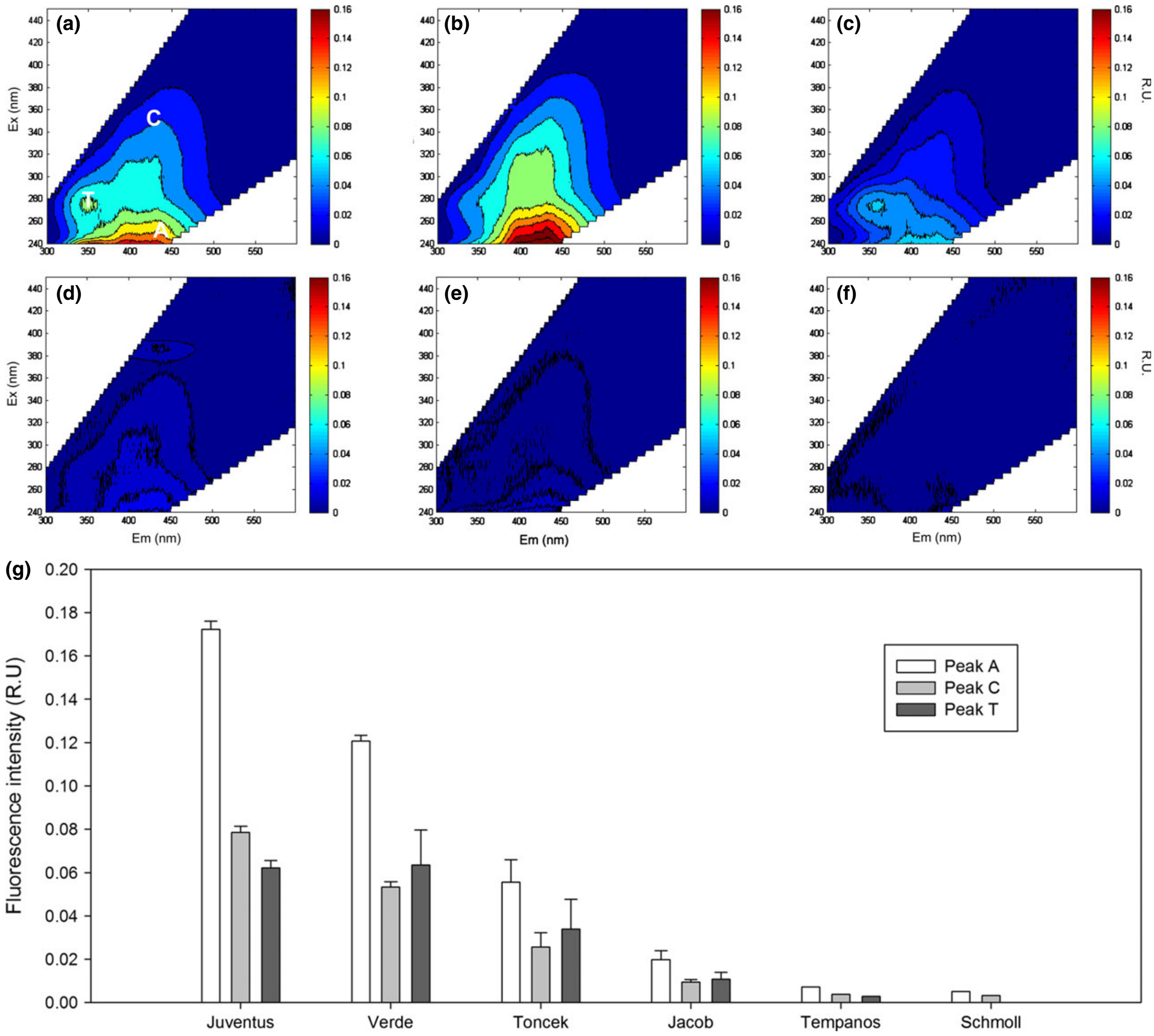

Fig. 4. Excitation and emission matrices (EEMs) from six study mountain lakes (a = Lake Verde; b = Lake Juventus; c = Lake Toncek; d = Lake Jakob; e = Lake Témpanos; f = Lake Schmoll; g = fluorescence intensity of the peaks corresponding to the three components A, C and T; A and C = humic peaks; T = protein-like peak).

0.6 and 0.8 indicate low recent DOM contribution to the DOM pool, likely attributable to low autochthonous production, being in agreement with the trophic condition reported in previous studies (Zagarese *et al.* 2000).

The excitation–emission matrices (EEMs) obtained from the water samples (Fig. 4a–f) indicated lakes Verde and Juventus displayed the highest fluorescence intensities, followed by lakes Toncek and Jakob (Fig 4a–d). Extremely low intensities were recorded for lakes Schmoll and Témpanos, being close to the detection limit (Fig. 4e,f). Following the procedure of Coble (1996), three distinctive fluorescence signals were detected. These included two humic-like fluorophores recognized as 'peak A' (Ex_{max}/Em_{max} 250–430 nm) and 'peak C' (Ex_{max}/Em_{max} 350–420 nm), and a fluorophore known as protein-like 'peak T' (Tryptophan-like; Ex_{max}/Em_{max} 270–350 nm) (Fig. 4g). Peaks A and C revealed the presence of humic material, generally associated with terrestrial sources, while the peak T usually has been related to autochthonous DOM (Coble 1996; Zhang *et al.* 2010; De Laurentiis *et al.* 2012). Although other fluorophores were described by Coble (1996) (i.e. 'Marine humic-like', 'Tyrosine-like'), it was difficult to clearly assign these other peaks in the present study using only the 'peak-picking' approach. Future studies that include a larger number of samples could allow for analysis of the commonly used parallel factor analysis (PARAFAC) to discriminate other fluorophores (Stedmon, *et al.* 2003).

The three peaks were recorded with relatively high intensities for lakes Juventus and Verde. Peaks A and C were comparatively higher than peak T, suggesting a main contribution of a humic component. Peak T was found to be similarly high for lakes Verde and Juventus. This pattern is likely associated with the higher autochthonous production of DOM in the case of Lake Verde, due to its mesotrophic condition (Fig. 4g). In contrast, the peak T for Lake Juventus could also be attributable to the presence of small phenols associated with tannins, as suggested by Maie *et al.* (2007), and probably derived from large phenolic compounds through photobleaching, noting that the samples were obtained at the end of the Austral summer. Moreover, other molecules containing an indole group may give the same signal as protein-like compounds, fluorescing in the Ex 287/Em 348 region (Aiken 2014). Conclusive evidence requires further analyses of water samples via techniques such as HPLC (high-performance liquid chromatography) and size exclusion chromatography.

Multivariate analysis: principal component analysis

The PCA included both limnological variables and DOM characteristics. The first two principal components explained 82.34% of the total variance. The first component (PC1) explained 67.23%, being correlated positively (>0.7) with altitude and S_R, while it was negatively correlated (>−0.7) with most of the remaining variables (i.e. % vegetation, electrical conductivity, TP, TN, DOC, peak A, peak C, peak T, a_{254} and a_{440}) (Fig. 5). The PC2 explained 15.10%, being correlated positively with SUVA (0.766), and negatively correlated with chlorophyll-*a* concentration (−0.64) (Fig. 5). The resulting plot of PC1 vs. PC2 indicated altitude and vegetation are the main factors contributing to the landscape position of the lakes. This analysis permitted discrimination of the studied lakes into two groups: (i) lakes located below the treeline (Verde and Juventus) and (ii) lakes located above the treeline (Toncel, Jakob, Témpanos and Schmoll). Furthermore, the PCA separated lakes Juventus and Verde, attributable mainly to differences in the chlorophyll-*a* and nutrient concentrations (Fig. 5). Altitude and vegetation cover then emerged as strong variables controlling the nutrient concentrations, as well as the DOM characteristics of the lakes along the landscape.

CONCLUDING REMARKS

Characterization of the DOM of the study lakes highlighted that a combination of CDOM and FDOM techniques provides a rapid initial insight into the origin and molecular weight of the DOM. The lakes, which were characterized through the coefficients a_{254} and a_{350}, the spectral slopes, the S_R and the HIX and BIX indices, appeared to be affected similarly by their catchments, with a greater contribution of allochtonous DOM, compared to the autochthonous DOM. Analysis of the EEMs could detect three different fluorophores attributable to two humic peaks (peaks A and C) and one protein-like peak (peak T), thereby again providing a greater resolution in detecting differences among lakes.

In regard to landscape integration, Lake Schmoll and Lake Témpanos can be considered high-altitude lakes, given their extremely low DOM concentrations and ultra-oligotrophic condition (Kratz *et al.* 2006; Mladenov *et al.* 2011). Lakes such as Toncek and Jakob, located lower in the landscape and on the treeline ecotone, also receive DOM inputs from the vegetation belt of the deciduous *krummholz* shrubs of *Nothofagus pumilio* and from the meadows to which they are marginally connected. Nevertheless, their DOC concentrations are very low, likely being subjected to photochemical reactions such as suggested by Zagarese *et al.* (2000) and Rose *et al.* (2009). Finally, lakes Juventus and Verde are located well below the treeline, clearly evidencing the contributions from their forested catchments. Lake Juventus receives DOM inputs from the mixed evergreen *Nothofagus dombeyii* forest, likely through run-off and possibly groundwater as well. Similarly, Lake Verde receives DOM contributions from the deciduous mixed *N.s pumilio* forest covering its catchment. Even though these two lakes are apparently similar in terms of the DOM features, other parameters such as TP, TN and chlorophyll-*a* concentrations indicate differences in their trophic state, with Lake Verde being mesotrophic and Lake Juventus being oligotrophic.

The low intensities of all the fluorophores in lakes Jakob, Témpanos and Schmoll generally reflect their extremely low DOC concentration, a very low contribution from their catchments, as well as low primary production. Lakes Juventus and Verde had the highest intensities of the three fluorophores, reflecting their higher DOC content, with a larger allochtonous input of DOM in both lakes, and a higher autochthonous production in the case of Lake Verde. An intermediate situation was observed for Lake Toncek, with moderate intensities of the three fluorophores reflecting the DOM contribution from the catchment, and an enhanced internal production

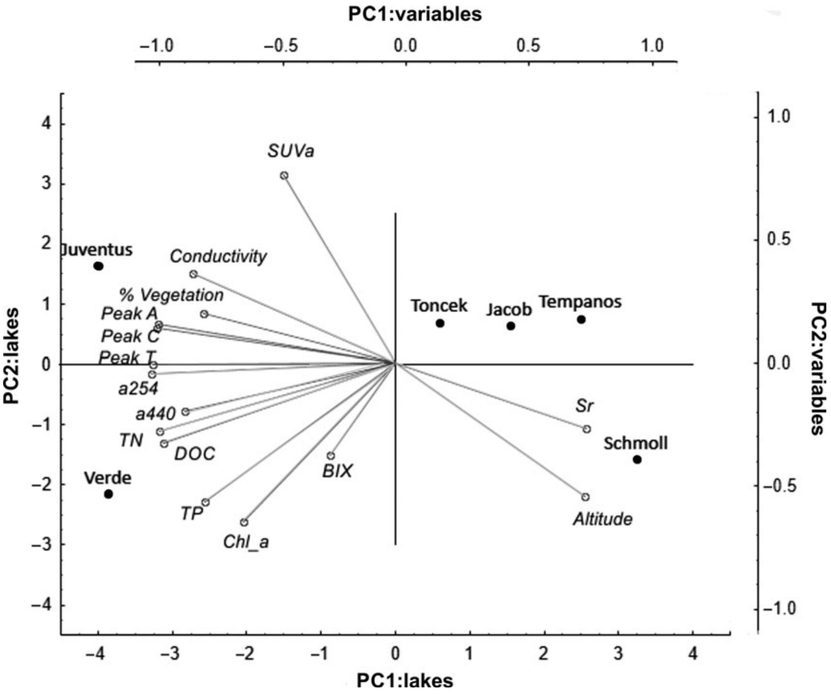

Fig. 5. Principal Component analysis (PC1 vs. PC2) depicting position of lakes in relation to the combination of limnological and dissolved organic matter parameters.

compared to Lake Jakob, the latter occupying a similar position in the landscape.

Overall, a combination of DOM characterization and water chemistry appears sufficient to understand the influence of the catchment at different landscape positions, even with very diluted water bodies such as the Andean mountain lakes in the present study. The present study appears to be the first study in Patagonia providing evidence of the interactions of terrestrial and aquatic systems in high mountain regions. Despite the small set of lake samples included in the present study, these analyses highlight their interactions with the catchment, allowing better understanding of the trophic condition of these lakes as indicated by their nutrient and chlorophyll-*a* concentrations. Sustained environmental assessments, including DOM and nutrient characterization in mountain lakes, can be useful in revealing the joint dynamics of these aquatic systems within their catchments. As the condition of lakes fluctuate with their surroundings, with remote lakes being extremely sensitive to changes in their catchments, they may accurately track the impacts of climate and anthropogenic changes on the landscape.

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