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Patterns of dissolved organic matter across the Patagonian landscape: a broad-scale survey of Chilean and Argentine lakes

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Abstract. Dissolved organic matter (DOM) is a complex mixture of carbon compounds from autochthonous and allochthonous sources. Dissolved organic carbon (DOC) concentrations and optical metrics of DOM provide clues as to the sources and processes affecting the DOM pool. Herein we provide the first broad-scale characterisation of DOM from Patagonian lakes across a strong west–east precipitation gradient. Fifty-eight lakes from Northern Patagonia (Argentina and Chile) plus six lakes from the Antarctic Peninsula were sampled during summer 2000–01. Six DOM metrics were evaluated: DOC absorbance at 254 nm (a_{254}) and 350 nm (a_{350}), DOC-specific absorbance at 254 nm (a_{254}/DOC) and 350 nm (a_{350}/DOC) and spectral slope between 275 and 295 nm ($S_{275–295}$). The DOM of Chilean maritime lakes and shallow (<15 m) Andean lakes exhibited terrestrial signatures and a pattern of variation consistent with their occurrence across the longitudinal precipitation gradient (i.e. $S_{275–295}$ increased, whereas a_{350}/DOC decreased from west to east). The contribution of allochthonous DOM was smaller in deep (>15 m) Andean lakes, which is consistent with their longer water retention time. Steppe lakes, mostly from endorheic basins, made up the most heterogeneous group with regard to DOM characteristics.

Additional keywords: climate change, ecosystem processes, limnology.

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Introduction

Dissolved organic matter (DOM) is a major driver of the structure and function of aquatic ecosystems. DOM is involved in many important photochemical and biological processes and, as such, is an integral part of biogeochemical cycles (Pace and Cole 2002; Couture *et al.* 2012). The DOM pool present in natural waters includes fulvic, humic and non-humic substances (McKnight *et al.* 2001; Mostofa *et al.* 2009) that originate from three major sources: terrestrial soils (allochthonous DOM), *in situ* production in surface waters (autochthonous DOM) and human activities (anthropogenic DOM; Benner 2003; Zhang *et al.* 2009*a*; Mostofa *et al.* 2013*a*).

Chromophoric DOM (CDOM) is the optically active component of DOM and is often a major fraction of the DOM pool (Aiken 2014); therefore, it is usually positively correlated with dissolved organic carbon (DOC) concentration (Ferrari 2000). CDOM absorbs light in the ultraviolet and blue regions of the spectrum (Kirk 1994; Morris *et al.* 1995; Helms *et al.* 2008). The optical properties of CDOM are tightly related to its origin (autochthonous *v.* allochthonous), molecular size and diagenetic state (Helms *et al.* 2008). The transformation of CDOM is determined by physical and biological processes such as inputs, biogeneration and photobleaching, which are primary sinks and sources of this DOM fraction (Zhang *et al.* 2009*b*). CDOM is affected by several factors, including DOM content and its chemical nature (Singh *et al.* 2010), the occurrence and quality of suspended particulate matter (Zhang *et al.* 2007; O'Donnell *et al.* 2010), salinity (Del Vecchio and Blough 2004; Jonasz and Fournier 2007) and photo-induced and microbial processes (Hernes and Benner 2003; Zhang *et al.* 2009*b*; Guillemette and del Giorgio 2011; Mostofa *et al.* 2013*b*). Assessing DOM through DOC concentration and CDOM spectral analysis (i.e. absorption coefficients, spectral slopes etc.) allows the comparative analysis of different water types, including evaluation of allochthonous and autochthonous C sources (Helms *et al.* 2008), the chemical composition and molecular size of dissolved organic compounds (Weishaar *et al.* 2003; Aiken 2014) and the transformation processes in the DOC pool (i.e. photochemical and biological; Osburn *et al.* 2001; Helms *et al.* 2008, 2014; Guillemette and del Giorgio 2011).

Lakes are sensitive ecosystems that integrate the effects of climate variability. Changes in the watershed and airshed of lakes are readily translated into physical, chemical and biological properties (Adrian *et al.* 2009; Williamson *et al.* 2009, 2014). DOM signatures can be studied and interpreted through optical CDOM proxies, uncovering internal processes as well as environmental events at the landscape level. Because the signals in the DOM pool of lakes integrate processes occurring at different temporal and spatial scales, they can be used to assess multiple ecological issues, such as carbon fluxes within catchments, the level of allochthony, the effect of climate forcing etc. (Adrian *et al.* 2009; Williamson *et al.* 2014; Forsström *et al.* 2015). The signals of weathering in the DOM pool include shifts in DOC concentration and DOM quality (Williamson *et al.* 2014).

The Patagonian region includes numerous lakes with different origins and evolutionary stages that are scattered in a variety of different landscapes. In particular, these lakes occur along a noticeable west–east gradient from the Pacific Ocean to the Atlantic coast (Jobbágy *et al.* 1995; Paruelo *et al.* 1998*a*, 1998*b*). This gradient is largely the result of the prevailing westerly winds bringing humidity from the Pacific to the continent. This results in a west–east continuum of the terrestrial biomes from lowland temperate forests on the Chilean side to a semidesert dominated by low shrubs in the Argentine steppe (Beard 1990; Paruelo *et al.* 1998*b*). Superimposed on this general west–east trend is an altitudinal gradient caused by the presence of the Andean Cordillera, resulting in a steep transition from a rainforest (in lowland areas) to bare rock (above the tree line), as well as in a strengthening of the longitudinal precipitation pattern (i.e. increased orographic precipitation on the Chilean flank and a rain shadow effect on the Argentine side; Jobbágy *et al.* 1995; Bianchi *et al.* 2016).

Knowledge of DOM patterns across naturally occurring environmental gradients provides clues as to the dominant mechanisms governing carbon flows into lakes, as well as on the process responsible for in-lake DOM changes, which, in turn, may help anticipate future lake responses to predicted environmental changes. Herein we provide the first broad geographic-scale characterisation of the DOM pool from Patagonian lakes across the sharpest part of the west–east precipitation gradient, including Chilean and Argentine sites. On account of the large heterogeneity that characterises Patagonia in terms of climate and landscape features, we were also interested in identifying sets of relatively homogeneous lakes in terms of DOM origin and processes that could eventually serve as potential sentinels of climate variability.

Materials and methods

Study area

Patagonia comprises land in the latitudinal range between 39 and 55°S. The Andean Cordillera is a major geographic feature of Patagonia that also serves as a natural border between Chile (west) and Argentina (east). In general, the climate of the region is governed by the strong westerly winds that, in combination with the north–south orientation of the Andes, determine a steep west–east precipitation gradient (Walter and Box 1983; Jobbágy *et al.* 1995; Paruelo *et al.* 1998*a*; Austin and Sala 2002). The uplift of humid air masses on the windward side leads to hyperhumid conditions along the Pacific coast and the western slope of the Andes, whereas the downslope subsidence dries the eastern plains creating arid, highly evaporative conditions (Paruelo *et al.* 1998*a*; Garreaud *et al.* 2013; Lenaerts *et al.* 2014; Bianchi *et al.* 2016). Northern Patagonia in particular encompasses different climates: a hyper-humid maritime climate along the Pacific coast, a humid temperate climate in the Andean stretch and a semi-arid and arid climate along eastern stretches (Paruelo *et al.*1998*a*; Garreaud and Falvey 2009; Garreaud *et al.* 2013). This is reflected in the vegetation, promoting a marked shift from closed canopy forests (Valdivian rainforest and humid temperate evergreen *Nothofagus* forest) towards a grass–shrub steppe and a desert scrub in the east (Paruelo *et al.* 1998*b*; Austin and Sala 2002). Remarkably, this sharp precipitation–vegetation gradient has been targeted, among others, at different locations worldwide as a model gradient for understanding large-scale controls of ecosystem processes (International Geosphere Biosphere Programme, http://www.igbp.net/, accessed 29 December 2016).

Along the described gradient, there are many lakes of different origins and typologies. Close to the coastal cordillera along the Pacific coast (Chile), several lakes occur close to sea level (10–250 m above sea level, ASL), surrounded by native forests and affected by their proximity to the ocean. On both sides of the Andes, there are deep and shallow lakes of glacial origin (Quirós and Drago 1999) along a steep altitudinal gradient, with small mountain lakes at high and mid altitudes (~900–2200 m ASL) and several large deep lakes and small and shallow systems at the piedmont (~200–700 m ASL), surrounded by native forests. These systems constitute the headwaters of the main hydrological networks of the region that collect snowmelt and precipitation water in the Andes, conducting it through the fluvial systems crossing the Patagonian steppe plains to the Atlantic Ocean or the steep slopes towards the Pacific Ocean. In the eastern part of Patagonia, there are many closed depressions of different types and sizes, including shallow depressions in soft sediments as well as hollows in the basaltic plateaux (Iriondo 1989).

For the present study, 58 lakes including freshwater and saline systems from Argentine northern Patagonia (provinces of Neuquén, Río Negro and Chubut) and Chile (Regions X and XIV) were surveyed once during summer (2000–01; Fig. 1; Table 1). The study area (approximately between 69–74°W and 39–46°S) encompasses several ecogeographic regions, spanning a wide range of elevation, precipitation, soil and vegetation types. Patagonian lakes were assigned to four groups according to their morphological and hydrological features as follows: (1) Chilean maritime lakes, occurring in areas of high rainfall close to the Coastal Cordillera (Chiloé Island and the surroundings of Puerto Montt); (2) deep (maximum depth >15 m) and (3) shallow (<15 m) Andean lakes located in the Andean stretch along a marked precipitation gradient from west (Chile) to east (Argentina) and surrounded by the Valdivian rainforest or by humid forests; and (4) steppe lakes occurring in the arid steppe at the east, which are mostly endorheic lakes. In addition, 18 water samples from six Antarctic lakes around Base Esperanza (63.2°S, 56.6°W; Argentina) were included for comparison. Considering the lack of soil development within the watershed of Antarctic lakes, water samples from these lakes were expected to contain exclusively autochthonous organic matter (Table 1).

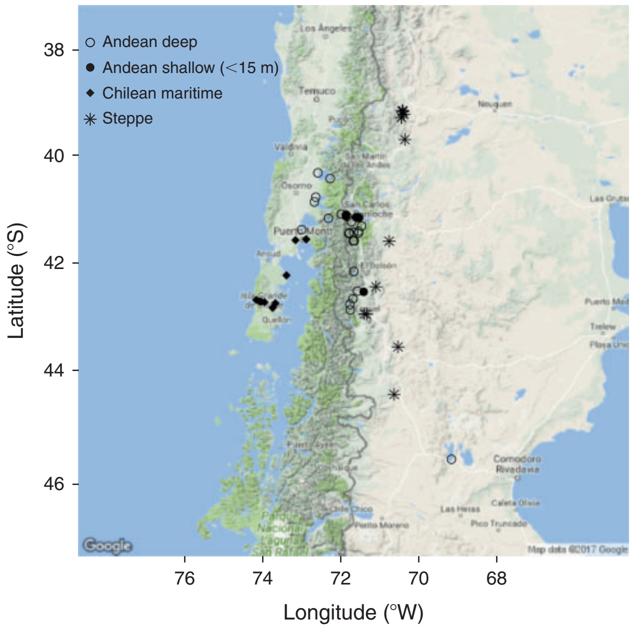

Fig. 1. Geographical location of the four groups of Patagonian lakes studied, namely the Chilean maritime, deep (>15 m) and shallow (<15 m) Andean and steppe lakes. Lakes from the Antarctic Peninsula are not shown.

Field sampling

Each lake was visited once in summer (2000 or 2001). Pelagic samples were collected at 2-m depth. Samples were immediately filtered through pre-ashed glass fibre-filters (Whatman, Maidstone, UK) and stored cold (~2°C). Several laboratory analyses were performed on each sample. Conductivity (Orion model 115, Analytical Technology Inc., Boston, MA, USA) and pH (VWR 3000; VWR Scientific, West Chester, PA, USA) were measured using bench-top meters. Alkalinity was measured using the Gran titration method described by Wetzel and Likens (1991). Total particulate material was measured using ashed, pre-weighed glass-fibre filters (pore size ~0.7 μm). After filtration, filters were placed in a 60°C drying oven for 24 h before being reweighed. Chlorophyll-*a* was measured using warm 90% ethanol extraction, corrected for phaeophytin (Marker *et al.* 1980; Nusch 1980).

Samples for DOM characterisation were passed through polysulfone (Sterivex 0.22 μm; EMD-Millipore, Bradford, MA, USA) filters. Each cartridge filter was prerinsed with 100 mL of deionised water before use. Dissolved absorbance measurements were made using either a Shimadzu UV-1601 dual-beam spectrophotometer (Shimadzu, Tokyo, Japan) or a HP 8453E spectrophotometer (Hewlett Packard, Waldbronn, Germany) using quartz cuvettes (path length 1, 5 or 10 cm, depending on sample absorbance). Samples were referenced to air and deionised water blanks were used to correct for scatter by

Table 1. Geographic, environmental, and dissolved organic matter features of the five groups of lakes studied, namely Andean deep and shallow, Chilean Maritime, steppe and Antarctic lakes

Data show mean values with the range (minimum–maximum) given in parentheses. Z_{max}, maximum depth; DOC, dissolved organic carbon; a_{254}, a_{350}, absorbance coefficients at 254 and 350 nm respectively; a_{254}/DOC, a_{250}/DOC, DOC-specific absorbance at 254 and 350 nm respectively; $S_{275–295}$, spectral slope between 275 and 295 nm

Variable (units)	Lake group				
	Andean deep ($n = 22–25$)	Andean shallow ($n = 7–8$)	Chilean Maritime ($n = 8–12$)	Steppe ($n = 3–13$)	Antarctic ($n = 3–13$)
Latitude (°S)	41.8 (40.3–45.6)	41.2 (41–42.5)	42.2 (41.4–42.8)	40.9 (39–44.4)	63.4 (63.4–63.4)
Longitude (°W)	71.8 (69.1–73)	71.6 (71.4–71.8)	73.5 (72.8–74.1)	70.6 (70.3–71.4)	57 (57–57)
Elevation (m)	496.9 (51–1000)	805 (550–1100)	87.1 (30–250)	1048.5 (550–1400)	59.4 (49–100)
Lake area (km^2)	190.6 (1.4–877)	6.5 (0.1–39.4)	10.1 (0.5–19.1)	6.9 (0.8–17)	0 (0–0.1)
Z_{max} (m)	179.4 (24–464)	9.2 (3.5–13)	25.5 (3–58)	5.5 (3–10)	4.4 (1.5–6.9)
Precipitation (mm year^{-1})	1786 (150–3400)	1975 (500–3400)	2166.7 (1700–2400)	330.8 (150–800)	1195.8 (1095–1700)
Conductance (μS cm^{-1})	66.4 (24.7–406)	69.5 (14–105.7)	395.9 (19.4–1765)	1179 (407–3940)	45 (12.7–142)
Alkalinity (μEq L^{-1})	483.8 (172–3504)	529.7 (96–831)	129.3 (23–283)	16 534 (21 80.5–59 972)	52.7 (24.3–103)
pH	7.4 (6.9–8.7)	7.2 (6.6–7.7)	6.7 (5.9–7.4)	9.1 (8.2–9.8)	6.1 (4.2–6.6)
Chlorophyll-*a* (μg L^{-1})	3.3 (0.2–51.7)	2.7 (0.4–12.2)	4.1 (1.2–12.7)	42.6 (1.1–170.7)	0.3 (0.2–0.5)
DOC (mg L^{-1})	0.8 (0.3–2.8)	2.8 (0.9–5.2)	5.5 (3–8.7)	83.8 (12.9–271)	0.4 (0.3–0.9)
a_{254} (m^{-1})	2.3 (1–10.5)	16.2 (3–40.1)	54.5 (12.7–97.5)	310.5 (46.7–913.2)	1.5 (0.6–3.4)
a_{350} (m^{-1})	0.3 (0.1–1.3)	3.4 (0.6–9.6)	13.4 (2.3–28.8)	35.5 (2.9–165.9)	0.4 (0.1–0.8)
a_{254}/DOC (L mg^{-1} m^{-1})	2.9 (1.4–5.7)	5.2 (3.3–7.8)	9 (4.1–11.2)	4 (1.7–6.6)	3.4 (2.1–6.4)
a_{350}/DOC (L mg^{-1} m^{-1})	0.4 (0.2–1.1)	1 (0.5–1.9)	2.3 (0.7–3.3)	0.5 (0–1.1)	0.8 (0.3–1.9)
$S_{275–295}$ (nm^{-1})	25.8 (18–38.2)	21.1 (17–26.7)	15.7 (13–21)	30.6 (21.5–47.3)	17.8 (12.6–25.3)

the cuvette. The absorption coefficient at specific wavelengths (a_λ, m^{-1}) was calculated according to Kirk (1994) as follows:

$$a_\lambda = (a_\lambda\,\text{sample} - a_\lambda\,\text{blank}) \times 2.303 \div \text{path length}$$

where the path length is measured in metres. Here we report absorbance at 254 nm (a_{254}) and 350 nm (a_{350}). The spectral slope for the range 275–295 nm ($S_{275-295}$) was calculated as the slope of the ln-transformed values of absorbance *v.* wavelength and used as a proxy of DOM molecular weight (inverse relationship; Helms *et al.* 2008; Fichot and Benner 2012). DOC concentration was measured using a Shimadzu TOC-5000 (Sharp 1993). Specific DOC absorbance at 254 nm (a_{254}/DOC) and 350 nm (a_{350}/DOC) was calculated by dividing the absorption coefficient by DOC concentration (mg L^{-1}) and used as a proxy of aromaticity and lignin content respectively (Weishaar *et al.* 2003; Spencer *et al.* 2009).

Statistical analyses

Principal component analysis (PCA) was used to reduce the dimensionality of the DOM dataset. DOM characteristics were analysed by means of variation partitioning to determine the unique and joint fractions of variation explained by the environmental and spatial components (Peres-Neto *et al.* 2006). Prior to the analysis, standard score transformations were applied to both the environmental variables (elevation, lake area, lake maximum depth, precipitation, conductance, pH) and DOM metrics (DOC, a_{254}, a_{350}, a_{254}/DOC, a_{350}/DOC and $S_{275-295}$) in order to correct for differences in scale (Zar 2010). Distance-based Moran's eigenvector maps (dbMEM; Dray *et al.* 2006) were used to obtain spatial predictor variables from the latitude and longitude coordinates of each lake. Following Dray *et al.* (2006), we first obtained a connectivity matrix (*B*) based on coordinates of sampling locations. The relative neighbourhood model (Borcard *et al.* 2011) was selected (Akaike information criterion, AIC) to define neighbouring sites. Then, we estimated the intensity of connections (i.e. the weighting matrix, *A*) using the default W-scheme (i.e. row-standardised spatial weights; Tiefelsdorf *et al.* 1999) provided in the 'nb2listw' function in the spdep package (R Foundation for Statistical Computing, Vienna, Austria). The final spatial weighting matrix (*W*) was obtained from the Hadamard (i.e. term-by-term) product of *B* and *A*. This final matrix was analysed with a PCA with resulting eigenvectors corresponding to spatial components (i.e. MEM variables), which represented orthogonal spatial patterns with higher and lower eigenvalues corresponding to broader- and finer-scale patterns respectively. Then, a forward selection was run to identify the significant spatial variables ($P < 0.05$ after 999 random permutations), using the double-step procedure proposed by Blanchet *et al.* (2008). In addition, we related DOM characteristics to the environmental dataset using redundancy analysis (RDA). Significant environmental explanatory variables were identified applying forward selection ($P < 0.05$ after 999 random permutations, double-step procedure). Finally, the selected environmental and spatial variables were used to perform partial RDAs of the variation partitioning by calculating adjusted R^2 values for each fraction (Peres-Neto *et al.* 2006).

All statistical analyses were performed in the R environment (R Foundation for Statistical Computing, Vienna, Austria) using the packages vegan (ver. 1.13-1, J. Oksanen, R. Kindt, P. Legendre, B. O'Hara, G. L. Simpson, P. Solymos, H. Stevens and H. Wagner, see http://vegan.r-forge.r-project.org/, accessed 21 March 2011), packfor (ver. 0.0–8/r99, S. Dray, P. Legendre and F. G. Blanchet, see http://R-Forge.R-project.org/projects/sedar/, accessed 2 June 2013), PCNM (principal coordinates of neighbourhood matrix, ver. 2.1-2/r109, P. Legendre, D. Borcard, F. G. Blanchet and S. Dray, see http://R-Forge.R-project.org/projects/sedar/) and spacemakeR, according to Borcard *et al.* (2011).

Results

The Patagonian lakes studied exhibited a wide range of water characteristics (Table 1). Conductance was lower in deep and shallow Andean lakes, as well as in lakes from the Antarctic Peninsula. In contrast, maritime Chilean lakes and Argentine steppe lakes exhibited much higher conductance. Alkalinity increased linearly with conductance in both deep and shallow Andean lakes and in steppe lakes. In contrast, the two more maritime groups (Chiloé Island plus Puerto Montt area and Antarctic) exhibited lower alkalinity at comparable conductance values (Fig. 2*a*). Deep and shallow Andean lakes had circumneutral pH, Chilean maritime and Antarctic lakes were slightly acidic and steppe lakes were markedly alkaline. There was a direct relationship between pH and ln alkalinity ($R^2 = 0.83$, $P < 0.0001$, Fig. 2*b*).

The lakes encompassed a wide range of DOC concentrations. Deep Andean lakes, as well as Antarctic lakes, had low DOC concentrations, typically below 1 mg L^{-1}. Shallow Andean lakes and Chilean maritime lakes had intermediate DOC concentrations, approximately within the 1–10 mg L^{-1} range, whereas most Argentine steppe lakes had DOC concentrations ranging from slightly less than ~10 up to 271 mg L^{-1} (Table 1; Fig. 3). In addition, the lakes exhibited a wide range of optical characteristics. Overall, a_{254} (data not shown) and a_{350} (Fig. 3*a*) increased with DOC. However, the pattern for different groups of lakes differed slightly; for example, at comparable DOC concentrations, the absorbance (both a_{254} and a_{350}) was stronger for Antarctic lakes and weaker for steppe lakes. Similarly, within the subset of data formed by Chilean maritime lakes, shallow Andean lakes and deep Andean lakes, $S_{275-295}$ appeared to be linearly and inversely related to DOC (Fig. 3*b*). Again, Antarctic and steppe lakes departed from this trend. Finally, the plot of DOC-specific absorbance *v.* DOC (Fig. 3*c*) showed a substantial amount of variability in a_{350}/DOC within Antarctic lakes and steppe lakes, but without exhibiting a distinct trend with DOC. In contrast, a_{350}/DOC increased with DOC in shallow Andean lakes and Chilean maritime lakes. In addition, there was substantial variability in the spectral slope ($S_{275-295}$). In all previous examples, Chilean maritime lakes and shallow Andean lakes exhibited rather similar trends, whereas deep Andean lakes have higher variability and fall closer to Antarctic lakes.

The results of the PCA performed with the six variables used to characterise the dissolved organic matter pool (DOC, a_{254}, a_{350}, a_{254}/DOC, a_{350}/DOC and $S_{275-295}$) are shown in Fig. 4. The first two principal components (PC1 and PC2) accounted for 46.8 and 41.78% of total variance. Within the plane defined by PC1 and PC2, Chilean maritime lakes, shallow Andean lakes and deep Andean lakes aligned from

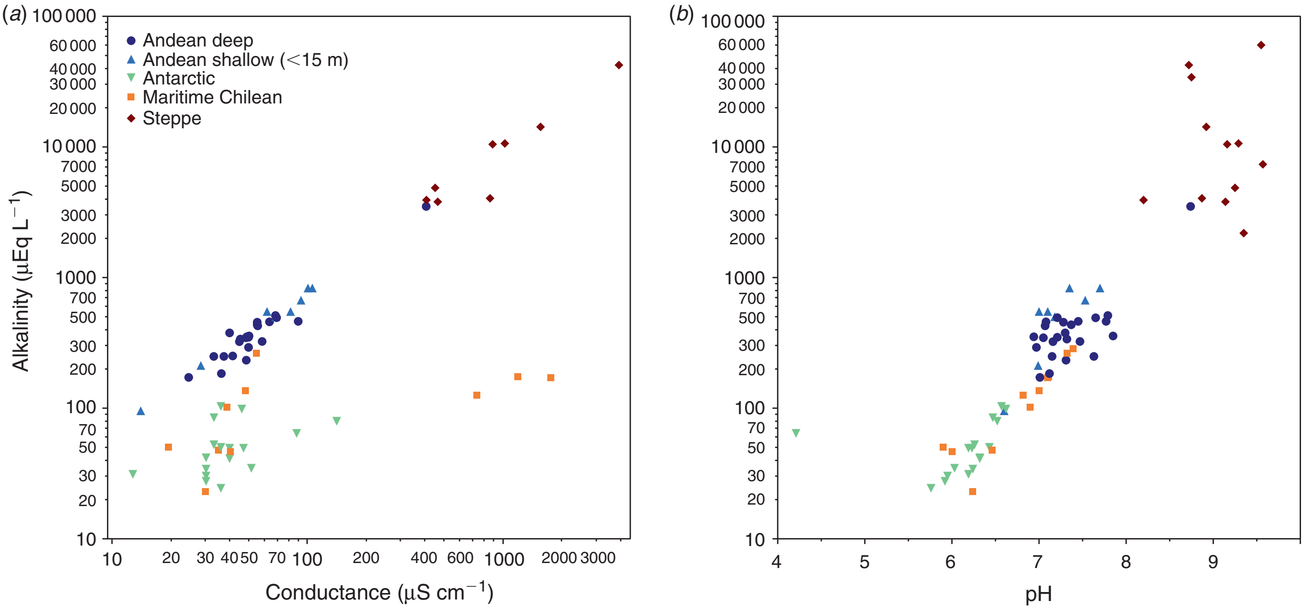

Fig. 2. Scatter plots of alkalinity *v.* (*a*) conductance and (*b*) pH in the Chilean maritime, deep (>15 m) and shallow (<15 m) Andean, steppe and Antarctic lakes.

upper left to lower right quadrants. Antarctic lakes aligned similarly, although slightly to the left of the previous three groups. Steppe lakes departed from the other groups of lakes and formed an amorphous conglomerate on the upper and lower right quadrants (Fig. 4). Notably, most of the variability in PC1 is due to this latter group of lakes.

Fig. 5 shows the distribution of the metrics used to characterise the DOM pool (DOC, a_{350}, a_{350}/DOC and $S_{275–295}$) along the predominant west–east gradient. DOC and a_{350} (as well as a_{254}; data not shown) exhibited a V-shaped pattern showing high values at either end of the gradient, whereas the lowest values corresponded to deep Andean lakes occurring on both sides of the Andean Cordillera (Fig. 5*a, b*). Conversely, a_{350}/DOC (and a_{254}/DOC; data not shown) exhibited an overall decreasing trend, whereas $S_{275–295}$ increased from west to east (Fig. 5*c, d*).

The dependency of DOM characteristics on the spatial and environmental traits of Chilean and Argentine (i.e. excluding Antarctica) lakes were assessed through variation partitioning analysis (RDA). This analysis showed that the set of environmental variables considered in the present study (elevation, mean annual precipitation, lake surface area, lake maximum depth, conductance and pH) were geographically structured at a broad spatial scale ($P_{\text{spatial model}} = 0.001$), but not at a fine spatial scale. The most relevant results are summarised below.

1. The first two axes of the RDA performed on spatial variables developed from the matrix of geographic coordinates accounted for 81.2% of total variation ($P_{\text{Axes 1 \& 2}} = 0.001$).
2. Forward selection of significant MEM variables selected for MEM 2, MEM 5 and MEM 11, all of which are associated with spatial trends at broad scales (Borcard *et al.* 2011).
3. Linear regression between environmental and spatial variables (i.e. the two first significant canonical axes) showed that elevation, maximum depth and conductivity exhibit the strongest spatial pattern. The first spatial RDA axis was significantly correlated with elevation and maximum depth ($P < 0.001$), whereas the second spatial axis was strongly correlated with conductivity ($P < 0.001$).
4. Finally, the environmental model selected for four of the five environmental parameters considered to explain DOM characteristics (i.e. pH, conductivity, maximum depth and elevation; $P_{\text{Environmental model}} = 0.001$) and the first two canonical axes accounted for 45.5% of total environmental variation ($P_{\text{Axes 1 \& 2}} = 0.001$).

In summary, the full model (i.e. including all significant environmental and spatial variables) accounted for 53% of total variation in DOM characteristics; environmental variables explained 45% (24% spatially structured), whereas pure spatial variables had a marginal effect of only 7% (Table 2).

Discussion

The set of lakes included in the present study occur within a broad geographic area of Chile and Argentina in the approximate region of 39–46°S, 69–74°W. Although the extent of the latitudinal and longitudinal coverage is similar, the most noticeable environmental gradient develops along the longitudinal dimension. As mentioned previously, this gradient in precipitation is the combined result of the prevailing westerly winds bringing humidity from the Pacific Ocean and the presence of the Andean Cordillera responsible not only for a reinforcement of the west–east rain gradient (orographic precipitation), but also for the added altitudinal gradient (Paruelo *et al.* 1998*a*). In the western extreme of the study area, Chilean maritime lakes occur in a hyper-humid region. These

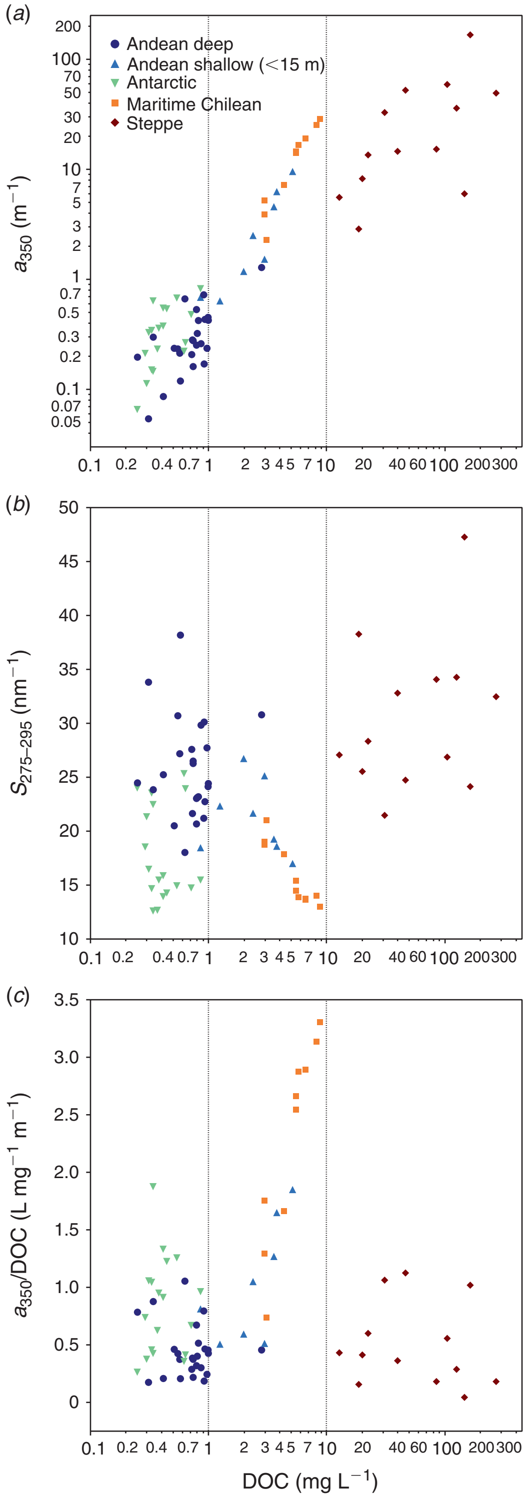

Fig. 3. Scatter plots of different optical parameters of lake dissolved organic matter plotted against dissolved organic carbon (DOC) concentration: (*a*) absorption coefficient at 350 nm (a_{350}), (*b*) spectral slope between 275 and 295 nm ($S_{275-295}$) and (*c*) the a_{350}/DOC ratio.

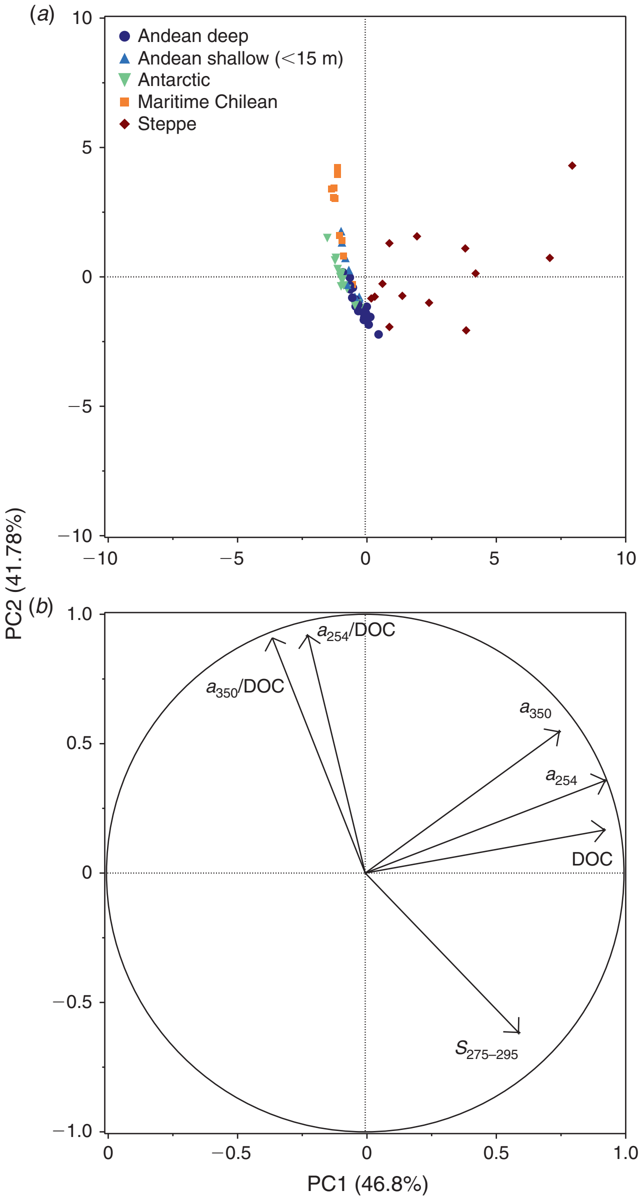

Fig. 4. Results from principal component analysis. (*a*) Scatter plot of the scores of the first two principal components (PC1 and PC2) performed on dissolved organic matter variables, namely dissolved organic carbon (DOC) concentration, absorption coefficient at 350 nm (a_{350}), the a_{350}/DOC ratio and the spectral slope between 275 and 295 nm ($S_{275-295}$). (*b*) Loading plot of primary variables on each principal component. a_{254}, absorption coefficient at 254 nm; a_{254}/DOC, DOC-specific absorbance at 254 nm.

lakes are humic (Villalobos *et al.* 2003) with evident marine influence (high conductance, but low alkalinity). As one moves east, there are several deep and shallow Andean lakes (Iriondo 1989) scattered along the aforementioned precipitation gradient (from 3000 mm year^{-1} in the west to 200 mm year^{-1} in the east; Bianchi *et al.* 2016) on both sides of the Andean Cordillera. Finally on the east end, most lakes in the arid Argentine steppe belong to endorheic basins (Iriondo 1989).

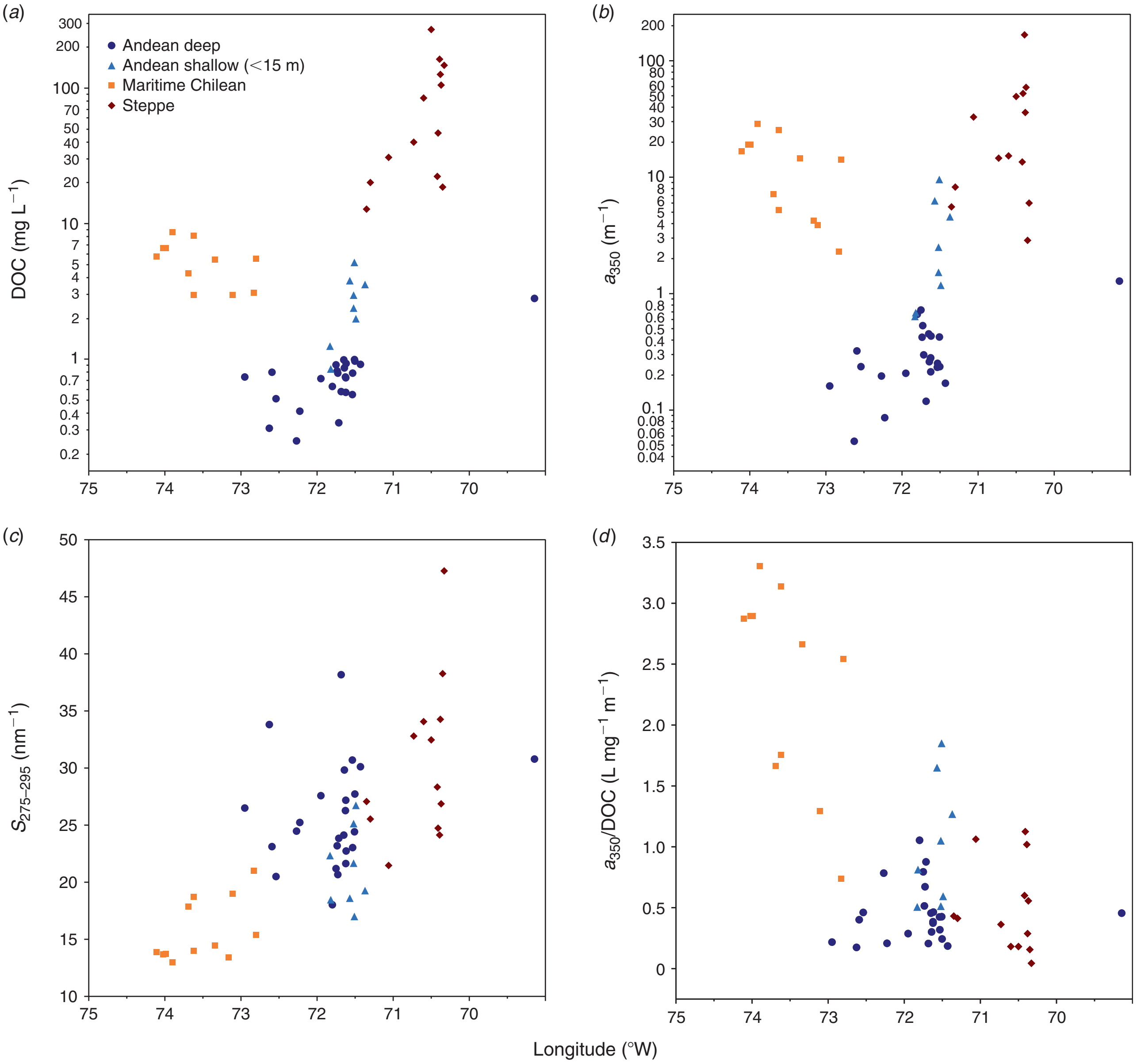

Fig. 5. Variation in the dissolved organic matter properties of the studied lakes across the longitudinal gradient. (*a*) Dissolved organic carbon (DOC) concentration, (*b*) absorption coefficient at 350 nm (a_{350}), (*c*) the spectral slope between 275 and 295 nm ($S_{275–295}$), and (*d*) a_{350}/DOC ratio.

Table 2. Variation in dissolved organic carbon (DOC) characteristics explained by environmental and spatial predictor variables using Moran's eigenvector maps (MEMs) and variance partitioning

Adjusted R^2 values represent the variation in DOC characteristics explained by environmental variables (E), environmental variables conditioned on spatial variation (E|S), spatial variables (S), spatial variables conditioned on environmental variation (S|E) and the total model including both environmental and spatial variables. $Z_{\max}$, maximum depth; Cond., conductance

n	Variables		Adjusted R^2 (*P*-value)				
	Environmental	Spatial	E	E|S	S	S|E	Total model
57	Elevation + $Z_{\max}$ + Cond. + pH	MEM 2 + MEM 5 + MEM 11	0.45 (0.001)	0.24 (0.022)	0.28 (0.001)	0.07 (0.094)	0.53 (0.001)

DOC and a_{350} exhibited a similar V-shaped longitudinal pattern. High values of DOC and a_{350} were observed in Chilean maritime lakes; initially, both variables decreased towards the east and reached the lowest values in deep Andean lakes, but from there on both variables increased, reaching their highest values in the steppe. Although high concentrations of DOM in Chilean maritime lakes are likely related to high terrestrial inputs from leachates of the surrounding hyper-humid forests, the high DOM concentrations of arid steppe lakes are most likely linked to the same evaporative concentration processes responsible for their high conductance (salinity). Previous studies have documented the role of evaporative processes in concentrating DOM in temperate saline lakes (Curtis and Adams 1995; Curtis 1998; Mulholland 2003; Anderson and Stedmon 2007; Osburn *et al.* 2011). In the present study, the range of DOC concentrations in steppe lakes was similar to that reported for lakes from the Great Plains in the US (Osburn *et al.* 2011), which rank among the highest DOC concentrations in inland waters (Sobek *et al.* 2007). Around the centre of the longitudinal gradient (i.e. on both sides of the Andean Cordillera) both process (terrestrial inputs or evaporation) are probably relatively weak, resulting in low DOC and a_{350} values. Similarly, samples from Antarctic lakes, which are taken here as a reference of non-terrigenous organic matter (Vincent *et al.* 2008), also had low DOC and a_{350} values. In contrast, a_{254}/DOC exhibited a decreasing trend from west to east, whereas $S_{275–295}$ increased from west to east, suggesting that both the aromaticity (a_{254}/DOC) and the mean molecular weight of the DOM pool decreases from west to east.

To further explore characteristics of the DOM pool, the relationships between the different metrics of DOM were first explored by plotting them in pairs and then by using multivariate methods. Considering the whole set of lakes (i.e. including the Antarctic lakes), a_{350} increased with DOC concentration. However, a_{350}/DOC varied among the different groups of lakes. The a_{350}/DOC quotient was lower than ~1.5 and varied haphazardly with DOC concentration for Antarctic, steppe and deep (>15 m) Andean lakes. In contrast, the a_{350}/DOC quotient exhibited an increase with DOC concentrations for shallow (<15 m) Andean lakes and Chilean maritime lakes.

The previous discussion suggests that, on the one hand, there is a significant amount of redundancy in the information provided by the different organic matter metrics and, on the other hand, the organic matter properties within this set of lakes are tightly related to lake position along the west–east longitudinal gradient and lake depth. To further analyse this dataset, we performed two types of multivariate analyses. First, we ran a PCA including the five DOM metrics, which reduced the dimensionality of the dataset. Second, we performed a variation partitioning analysis that explicitly considered the space distribution of the Patagonian lakes studied (i.e. Antarctic lakes were not considered in this analysis).

Together, the first three PCs accounted for 95.4% (46.8, 41.7 and 6.9%) of total variance. This confirms that there is a substantial amount of redundancy between the variables selected to characterise the DOM pool. In the plot of the first two PCs: (1) Chilean maritime lakes and shallow Andean lakes formed an arrangement that is approximately to the a_{254}/DOC–$S_{275–295}$ axis (i.e. from high to low aromaticity and molecular weight); (2) Antarctic lakes, and to a lesser extent deep Andean lakes, diverge from the previous group towards lower DOC values; and (3) steppe lakes depart from the previous groups towards higher DOC and a_{350} values. The PCA also showed that differences in PC1, which by itself captures nearly half the total variance, are due mostly to variability within the steppe lakes group. In fact, if the first three PCs are plotted on a three-dimensional perspective (data not shown), virtually all data points, except the steppe lakes, plot within the PC2–PC3 plane. This suggests that the sources and process affecting the DOM pool in the steppe lakes group differ markedly from those governing DOM dynamics in the other four groups of lakes. Clearly, steppe sites make up the most heterogeneous group of lakes in terms of DOM characteristics. Most of these lakes belong to hydrologically isolated, endorheic basins, a fact that probably contributes to explaining the lack of a common pattern of variability.

In contrast, it is apparent that within Chilean maritime lakes and shallow Andean lakes the properties of the DOM pool vary systematically with increases in DOC. We suggest that for these two groups of lakes the primary source of DOM is terrestrially derived. Under this scenario, the high precipitation rates prevailing in the west are likely to translate into higher run-off and shorter water retention time (WRT; Kellerman *et al.* 2014), resulting in higher fresh allochthonous DOM inputs (high a_{350}/DOC, low $S_{275–295}$), with potentially high photoreactivity (see Anderson and Stedmon 2007; Osburn *et al.* 2011). Conversely, as precipitation decreases to the east, DOM inputs will decrease, and the resulting longer WRT would favour the loss of DOC-specific absorbance through in-lake degradation processes, including photobleaching (Kellerman *et al.* 2014). Such a mechanism may account for the patterns of optical characteristics of DOM *v.* DOC observed within Chilean maritime and shallow Andean lakes. Finally, although the source and processes affecting the DOM pool in deep Andean lakes may differ slightly, they also seem controlled by water inputs. Due to their much greater volume, WRT is likely to be much longer (Nõges 2009; Hanson *et al.* 2011; Brooks *et al.* 2014); therefore, the relative contribution of allochthonous terrestrially derived DOM would be smaller than in the previous two groups of lakes (Rasmussen *et al.* 1989). All in all, both groups of Andean lakes (shallow and deep) provide a convenient range of DOM characteristics that appear to be controlled by similar environmental process, although they may have different outcomes depending on lake morphometry (Rasmussen *et al.* 1989). These groups of lakes occur in a narrow longitudinal range and share similar origins, soils and vegetation types in the surrounding watersheds.

The previous analysis shows a substantial amount of variability in the chemical and optical characteristics of the DOM pool within the set of lakes studied. The variation partitioning analysis evidenced a strong environmental control of DOM. In turn, the spatial structure of environmental variability, mostly related to lake morphology and watershed hydrological characteristics, produces a similar spatial structure in DOM features. In particular, there is a marked gradient in DOM attributes from humic Chilean maritime lakes to shallow Andean lakes. We believe that this gradient results from a continuum consisting of high inputs of fresh terrestrial organic matter and short WRT at the Chilean maritime lake end to lower inputs of terrigenous organic matter and longer WRT in the deep Andean lake end.

Fresh terrestrial organic matter inputs would tend to increase DOC-specific absorbance (a_{350}/DOC) and decrease the spectral slope ($S_{275–295}$; Anderson and Stedmon 2007; Helms *et al*. 2008, 2014; Fichot and Benner 2012). In lakes where most DOM is of terrestrial origin, short WRT would translate into large supplies of DOM characterised by high a_{350}/DOC and moderate $S_{275–295}$ (Anderson and Stedmon 2007). In contrast, long WRT would result in lower supplies of DOC, which would undergo in-lake photobleaching for longer periods of time, resulting in lower a_{350}/DOC and steeper $S_{275–295}$ (Anderson and Stedmon 2007; Helms *et al.* 2008, 2014; Fichot and Benner 2012). Moreover, as WRT increases, the relative contribution of autochthonous DOM will tend to increase at the expense of DOM of terrestrial origin (Osburn *et al.* 2011).

Several recent studies have reported negative precipitation trends in Northern Patagonia (Nuñez *et al.* 2009; Villalba *et al.* 2012; Garreaud *et al.* 2013; Barros *et al.* 2015). The effects of decreased precipitation on Patagonian terrestrial ecosystems (particularly the temperate forests on both sides of the Andes) have been repeatedly addressed (Suárez and Kitzberger 2008; Álvarez *et al.* 2015; Camarero and Fajardo 2017; Dieguez and Paruelo 2017). In contrast, the potential effects of reduced rainfall on Patagonian freshwaters have been largely overlooked. We believe that the set of Chilean maritime lakes and Andean lakes provides a convenient observational system to investigate the effects of contemporary climate change. We hypothesise that decreasing precipitation will result in lower rates of terrestrial inputs into the aquatic ecosystems, through decreased run-off and increased WRT. The anticipated increase in water transparency has potential for affecting the functioning of the whole aquatic system (Williamson *et al.* 2014).

Conflicts of interest

The authors declare that they have no conflicts of interest.

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